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ORIGINAL

Precious Metals Recovery From Low-Grade Resources

Proceedings: Bureau of Mines Open Industry Briefing Session at the National Western Mining Conference, Denver, CO, February 12, 1986

Compiled by Staff, Bureau of Mines

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
Robert C. Horton, Director

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PREFACE

Most of the papers included in this Information Circular were presented at a Bureau of Mines open industry briefing held in conjunction with the National Western Mining Conference on February 12, 1986, in Denver, CO. The Bureau often sponsors meetings of this nature in an effort to move new technology into industry practice by drawing attention to developments that may solve certain problems or improve upon current techniques. Those desiring more information about Bureau research programs should contact the Bureau of Mines, Branch of Technology Transfer, 2401 E Street, NW, Washington, DC 20241.

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CONTENTS

	Page
Preface	i
Abstract	1
Introduction	1
Ion-Exchange Research in Precious Metals Recovery, by Glenn R. Palmer	2
Staged Heap Leaching-Direct Electrowinning, by C. H. Elges and M. D. Wroblewski	10
Mercury Precipitation During Cyanide Leaching of Gold Ores, by Richard G. Sandberg	19
Carbonaceous Gold Ores, by B. J. Scheiner	26
Carbon Adsorption-Desorption, by J. A. Eisele	34
Heap Leaching, by J. A. Eisele	37
The Carbon-in-Pulp Process, By Stephen D. Hill	40
Precious Metals Recovery From Electronic Scrap and Solder Used in Electronics Manufacture, by B. W. Dunning, Jr	44

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A	ampere
A/ft^2	ampere per square foot
A/in^2	ampere per square inch
°C	degree Celsius
cm	centimeter
cm^3	cubic centimeter
ft	foot
g	gram
gal	gallon
g/cm^3	gram per cubic centimeter
g/L	gram per liter
g/mt	gram per metric ton
h	hour
in	inch
kg	kilogram
kg/mt	kilogram per metric ton
kW•h/st	kilowatt hour per short ton
L	liter
lb	pound
lbf/in^2	pound (force) per square inch
lb/st	pound per short ton
lb/(st•h)	pound per short ton per hour
L/min	liter per minute
mg	milligram
mg/L	milligram per liter
mg/min	milligram per minute
mg/(min•g)	milligram per minute per gram
min	minute
mL	milliliter
mL/min	milliliter per minute
mm	millimeter
mt	metric ton
pct	percent
ppm	part per million
st	short ton
st/d	short ton per day
st/wk	short ton per week
tr oz	troy ounce
tr oz/st	troy ounce per short ton
V	volt
vol	volume
wt pct	weight percent
yr	year

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PRECIOUS METALS RECOVERY FROM LOW-GRADE RESOURCES

Proceedings: Bureau of Mines Open Industry Briefing Session
at the National Western Mining Conference,
Denver, CO, February 12, 1986

Compiled by Staff, Bureau of Mines

ABSTRACT

This information circular describes research the Bureau of Mines has conducted to improve technology for recovering precious metals from low-grade resources. Many of the reported findings are recent, and some of the work described is ongoing. Topics discussed include cyanidation of carbonaceous gold ores to enhance gold recovery, a new method for precipitating mercury during cyanide leaching of gold ores, a staged heap leaching process to generate suitable solutions for direct electrowinning of gold, the use of anion-exchange resins to recover gold from cyanide solutions, and precious metals recovery from electronic scrap.

INTRODUCTION

Although U.S. gold and silver resources are extensive, many of these resources are extremely low in grade and cannot be developed economically with conventional mining and mineral processing methods. By developing more efficient and economical mineral recovery techniques, the Bureau of Mines has helped to make these low-grade resources more accessible. Past research by the Bureau focused on the carbon adsorption-desorption, carbon-in-pulp, oxidation pretreatment, and heap leaching technologies used in various phases of precious metals recovery. Current research highlights even more economical and effective approaches to gold and silver recovery, such as the use of ion-exchange resins, staged heap leaching followed by direct electrowinning, and mercury precipitation from leach solutions. The results of the Bureau's research in these areas, including both past and current work, are presented in the following papers.

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ION-EXCHANGE RESEARCH IN PRECIOUS METALS RECOVERY

By Glenn R. Palmer[1]

ABSTRACT

The Bureau of Mines investigated the use of ion-exchange technology in the recovery of precious metals from cyanide leach solutions. Strong-base resins such as Amberlite IRA-430 are nonselective, and using them results in high metal loading of precious metals and mercury, but generally they are difficult to strip. Research was conducted to devise a sequential stripping technique for various strong-base anion-exchange resins. The sequential stripping of IRA-430, for example, eluted 100 pct of the mercury with 2N H_2SO_4, 100 pct of the silver with 200 g/L NaCl in 1N HCl, and all of the remaining gold with 0.75 pct NaClO in 150 g/L plus 5 g/L NaOH.

Weak-base resins generally are selective and yield low metal loading, but are not difficult to strip. Research was conducted to examine the possible application of various weak-base anion-exchange resins in the extraction of gold and/or mercury from a cyanide solution. Batch equilibrium experiments were performed at different pH values to evaluate which resins might show promising results in an actual mill circuit. Three experimental resins may have possible application because of their effectiveness in the pH range of 10 to 12. One of these resins, when tested with actual mill solutions in a flow-through column experiment, loaded to about 140 tr oz/st Au and produced a peak eluant concentration of 35 ppm Au.

INTRODUCTION

Numerous cyanide leach carbon-in-pulp (CIP), carbon-in-column (CIC), and carbon-in-leach (CIL) milling facilities have been constructed to process low-grade gold-silver ore deposits throughout the Western United States (1-9).[2] The use of activated carbon has greatly improved the efficiency of gold recovery operations. However, several drawbacks are inherent with the use of activated carbon:

1. Used carbon must be thermally reactivated to maintain its effectiveness (10-11).

2. Carbon loading may be inhibited by the adsorption of $CaCO_3$, organic reagents, and clay-type minerals.

3. Carbon stripping must be performed in a pressurized vessel at elevated temperatures, 120° to 130° C, to shorten the stripping time.

An alternative recovery technology studied by the Bureau of Mines involves the application of anion-exchange resins for the recovery of gold from cyanide solutions. As early as 1949 (11-13), attempts were made to use both weak- and strong-base anion-exchange resins. Since that initial work, various applications and problems associated with anion-exchange resins have been examined.

Strong-base resins are generally less selective for precious metals, but have higher loading capacities and are much less affected by pH than weak-base

[1]Metallurgist, Salt Lake City Research Center, Bureau of Mines, Salt Lake City, UT.

[2]Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

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resins. A general mechanism for loading a strong-base resin is as follows:

$$\vdash NR_3^+X^- + M(CN)_2^- \rightleftarrows \vdash NR_3^+M(CN)_2^- + X^-, \quad (A)$$

where $\vdash$, NR_3, H^+X^-, and $M(CN)_2^-$ represent the polymeric resin matrix, functional group, acid, and metal-cyanide complex, respectively. Weak-base resins are generally more selective for precious metals, but have lower loading capacities. Because protonation is required to extract anions, a pH of less than 10 is usually required (14). A general mechanism for loading a weak-base resin may be represented by the following:

$$\vdash NR_2 + H^+ + X^- \rightleftarrows \vdash NR_2H^+X^- \quad \text{(Protonation)} \quad (B)$$

$$\vdash NR_2H^+X^- + M(CN)_2^- \rightleftarrows \vdash NR_2H^+M(CN)_2^- + X^- \quad \text{(Loading)} \quad (C)$$

Both resin types can be eluted at ambient temperature and pressure. Weak-base resins generally can be eluted using a dilute caustic solution. Strong-base resins, however, are more difficult to elute and require a more rigorous treatment. Potassium thiosulfate, acetone plus HCl, ethyl acetate plus HNO_3 diluted with water (13), zinc cyanide, and dimethyl formamide have each been used to recover gold (15). Each elution technique has one or more of the following disadvantages: fire hazard, noxious gas formation, or the need for special regeneration procedures. The mechanisms for eluting strong- and weak-base resins are described by the reverse of reactions A and C, respectively.

STRONG-BASE RESINS

During the past few years, the Bureau of Mines has investigated problems associated with the elution of gold, silver, and mercury from strong-base resins such as Amberlite IRA-430 and 900 and Dowex 21-K, SBR, and SMA-1.[3] Tests were initiated by loading resins with 145 tr oz/st each of gold, silver, and mercury from cyanide solutions doped with radioactive tracers for analysis. The loaded resins were eluted with several eluants, such as H_2SO_4, HNO_3, acid chloride, hypochlorite, and/or alkaline chloride solutions.

Figure 1 shows a simplified flowsheet for the preferred eluting sequence. Table 1 presents the results of using the simplified flowsheet with each of the five resins. Generally, all five strong-base resins behaved similarly. Within the first 3 h, 100 pct of the mercury was eluted with 2N H_2SO_4. No gold and only about 10 pct of the silver was eluted with the mercury; however, about 20 pct of the silver was eluted with the mercury using the SBR resin. A subsequent elution with 200 g/L NaCl in 1N HCl removed all of the remaining silver from the five resins in 6 h with less than 10 pct of the gold being eluted. A final elution with 0.75 pct NaClO in 150 g/L NaCl plus 5 g/L NaOH removed 93 to 98 pct of the gold in 9 h.

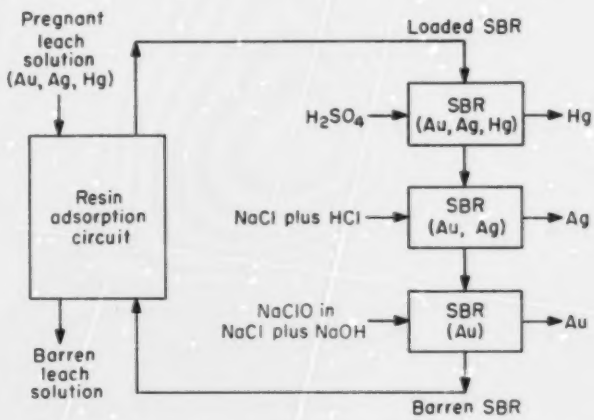

FIGURE 1. - Flowsheet for recovery of mercury, silver, and gold from a loaded strong-base exchange resin (SBR) by sequential elution.

[3]Reference to specific products does not imply endorsement by the Bureau of Mines.

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TABLE 1. - Sequential elution of mercury, silver, and gold from strong-base ion-exchange resins

Eluant solution	Cumulative elution time, h	Metal eluted (cumulative), pct														
		Amberlite IRA-430			Amberlite IRA-900			Dowex 21K			Dowex SMA-1			Dowex SBR		
		HG	Ag	Au	Hg	Ag	Au	Hg	Ag	Au	Hg	Ag	Au	Hg	Ag	Au
2N H_2SO_4.....	1	82	0	0	93	0	0	78	4	0	56	3	0	62	18	0
	2	98	0	0	92	0	0	99	6	0	87	5	1	95	18	0
	3	100	0	0	100	5	0	100	7	0	100	9	0	100	20	0
200 g/L NaCl in 1N HCl.....	4	100	62	0	100	65	0	100	69	0	100	57	2	100	62	0
	5	100	85	2	100	89	0	100	88	0	100	84	2	100	83	0
	6	100	95	5	100	97	0	100	96	1	100	93	2	100	93	0
	7	100	98	7	100	99	0	100	98	2	100	96	5	100	97	3
	8	100	100	8	100	100	0	100	100	4	100	98	5	100	99	3
	9	100	100	8	100	100	0	100	100	4	100	99	5	100	100	3
0.75 pct NaClO in 150 g/L NaCl plus 5 g/L NaOH.....	10	100	100	75	100	100	83	100	100	31	100	100	28	100	100	68
	11	100	100	83	100	100	91	100	100	58	100	100	56	100	100	79
	12	100	100	87	100	100	95	100	100	79	100	100	67	100	100	87
	13	100	100	87	100	100	95	100	100	91	100	100	76	100	100	90
	14	100	100	88	100	100	97	100	100	93	100	100	85	100	100	91
	15	100	100	89	100	100	97	100	100	95	100	100	92	100	100	92
	16	100	100	91	100	100	97	100	100	96	100	100	98	100	100	94
	17	100	100	92	100	100	97	100	100	96	100	100	98	100	100	94
	18	100	100	93	100	100	98	100	100	97	100	100	98	100	100	95

WEAK-BASE RESINS

In addition to the work on sequential elution of strong-base resins, research was conducted with weak-base resins to determine their effectiveness in adsorbing gold and/or mercury from a caustic-cyanide solution. Both commercially available and experimental anion-exchange resins were examined. Experimental resins were included in the investigation because they effectively adsorb metal-cyanide complexes in the pH range in which most gold mills operate, pH 10 to 11. Table 2 lists the weak-base resins tested in this investigation, along with available information concerning the resin matrix material and functional group.

TABLE 2. - Weak-base ion-exchange resins used in adsorption-elution experiments, by manufacturer

Resin	Functional group	Matrix
Sybron Corp.: A-305.....	Polyamine.....	Epoxy amine.
Diamond Shamrock Chemical Co:		
A-7.....	Secondary amine.....	Phenoformaldehyde.
A-340.....	Polyamine.....	Epoxy amine.
A-561.....	...do.....	Phenoformaldehyde.
Dow Chemical Co.:		
MWA-1.....	Dimethyl tertiary amine..	Styrene-DVB.
WGR-2.....	Polyamine.....	Epoxy amine.
XFS-40114.....	...do.....	Do.
XFS-43309.....	NA.....	NA.
XFS-43356.....	NA.....	NA.
XU-40138.....	NA.....	NA.
XU-40139.....	NA.....	NA.

NA Proprietary data not available from manufacturer.

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Batch-contact equilibrium experiments were performed with each ion-exchange resin to determine the effect of pH on the resin adsorption of gold and/or mercury. Six 1-g samples of each resin were equilibrated at a specific pH value between 5 and 13 with NaOH and HCl. A synthetic feed solution (200 mL) containing 500 ppm Au, 500 ppm Hg, and 0.5 g/L NaCN was placed in a 250-mL plastic digestion vessel, and the solution pH was adjusted to the respective pH of each resin. Resin was added and the mixture was rolled for about 48 h. Following the equilibrium contact, a sample of solution was removed for gold and mercury analysis, and the final equilibrium pH was measured.

Figures 2 and 3 show the adsorption results for gold and mercury, respectively, for the commercially available resins A-305, A-7, A-340, A-561, MWA-1, and WGR-2 (as listed in table 2). The slopes of these curves are very typical for weak-base resins and show clearly the influence of pH on a resin's ability to adsorb metal-cyanide complexes. Better adsorption occurred in the pH range below 9 for both gold and mercury, with none of the resins selective for gold over mercury. However, the A-305 resin indicated a preference for loading mercury over gold.

Additional research performed on the A-305 resin indicated that this resin may be suitable for application in adsorbing mercury from existing gold operations. Testing was expanded with a mill leach solution to determine the effect of adsorption-elution recycling using a flow-through column and an experimental procedure. Figure 4 presents typical adsorption curves for both gold and mercury using this resin. Initially, gold adsorbed onto the resin, then quickly desorbed into the solution. Mercury, however, steadily adsorbed. During the recycling experiments, the data showed that the resin's effectiveness to adsorb mercury decreased with each successive loading cycle. Attempts to regenerate the resin were unsuccessful.

Subsequently, several experimental resins were tested using the batch-contact equilibrium technique previously described. Figures 5 and 6 show the adsorption results for gold and mercury, respectively, for a group of experimental resins developed by Dow Chemical Co. (XFS-40114, XFS-43309, XFS-43356, XU-40138, and XU-40139). Of particular interest are the three resins XFS-40114, XU-40138, and XU-40139. Gold and mercury were more efficiently adsorbed by these three resins, at a pH between 9 and 11, than they were by any of the other previously examined resins. Also, the slopes of the curves for these resins were much steeper between pH 11 and 12, indicating that the resins should be easily eluted by a solution with a high pH value. Following the adsorption tests, a sample of XFS-40114 was eluted using 1M NaOH at ambient temperature. Nearly 100 pct of the gold and 50 pct of the adsorbed mercury were recovered with 100 mL of eluant.

Testing was expanded to determine the effectiveness of the three promising resins with actual leach solutions in a flow-through contact column. The leach solution contained 1.7 ppm Au, 3.0 ppm Ag, and 0.3 ppm Hg, with a pH of approximately 10.5 and a free cyanide concentration of 0.5 g/L. Approximately 5 L of solution was pumped through 1 g of resin in a 1-cm-ID glass column at a flow rate of 0.5 bed volume per minute. Following the adsorption phase, the loaded resin was eluted with 200 mL of 1M NaOH at a flow rate of 0.17 bed volume per minute. Adsorption curves for gold, silver, and mercury are shown in figures 7, 8, and 9, respectively. The total adsorption and elution recoveries for these experiments are given in table 3.

TABLE 3. - Summary of adsorption-elution results for selected resins, pct

Resin	Metal adsorption			Metal eluted		
	Au	Hg	Ag	Au	Hg	Ag
XFS-40114	54.2	51.8	4.8	13.7	0	76.6
XU-40138	57.7	57.4	10.8	53.1	8.7	85.1
XU-40139	81.1	66.6	13.2	13.1	6.0	51.9

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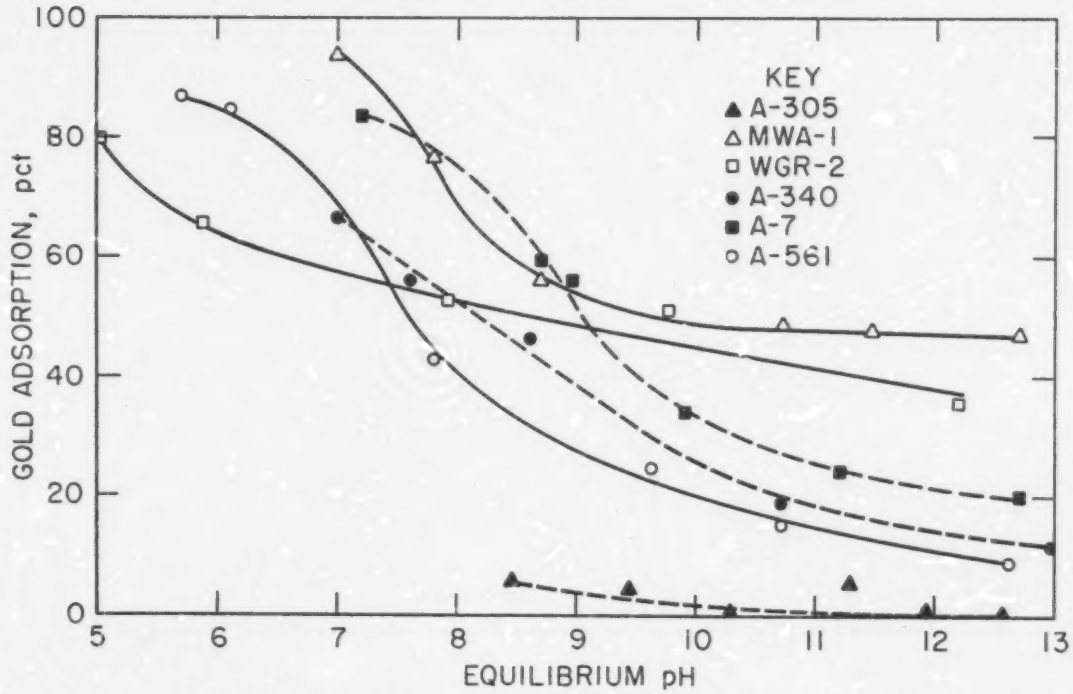

FIGURE 2. - Equilibrium adsorption curves for gold with commercially available exchange resins. (Broken curve patterns used for visual distinction only.)

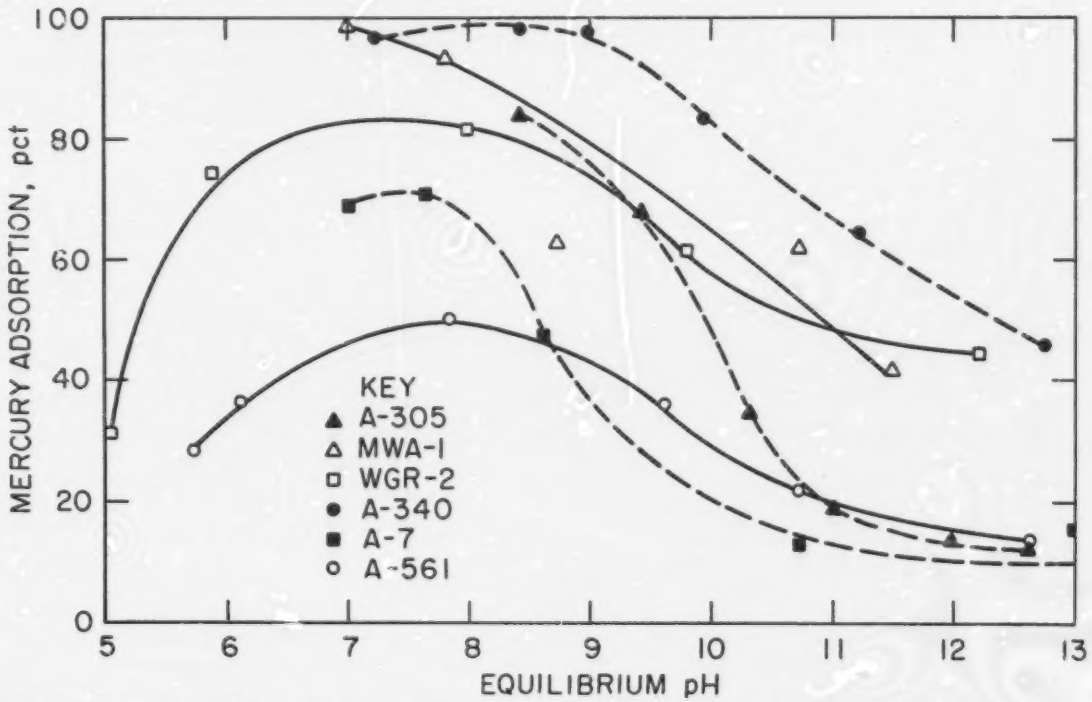

FIGURE 3. - Equilibrium adsorption curves for mercury with commercially available exchange resins. (Broken curve patterns used for visual distinction only.)

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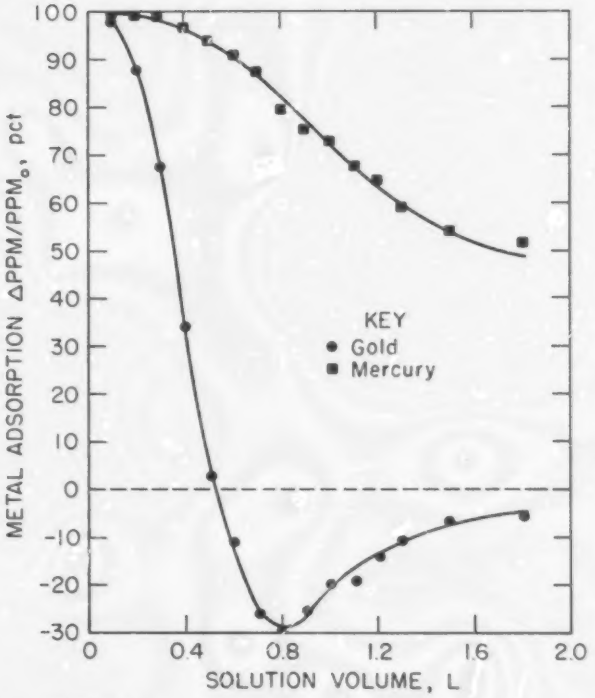

FIGURE 4. - Gold and mercury adsorption curves using resin A-305 with actual leach solution.

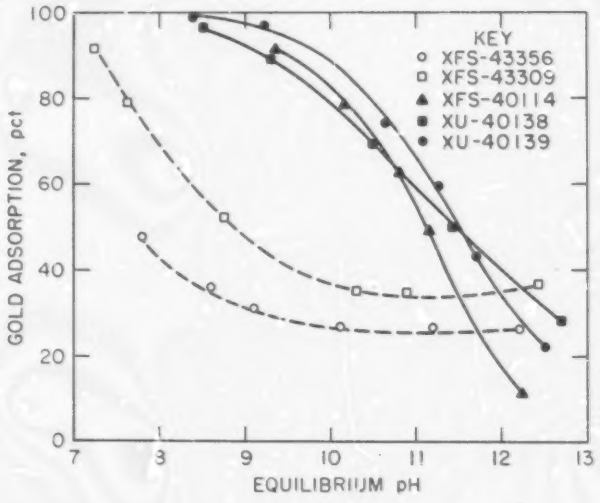

FIGURE 5. - Equilibrium adsorption curves for gold with experimental exchange resins.

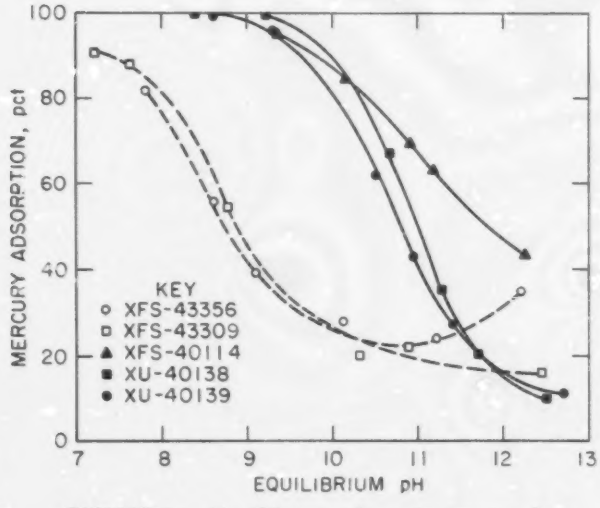

FIGURE 6. - Equilibrium adsorption curves for mercury with experimental exchange resins.

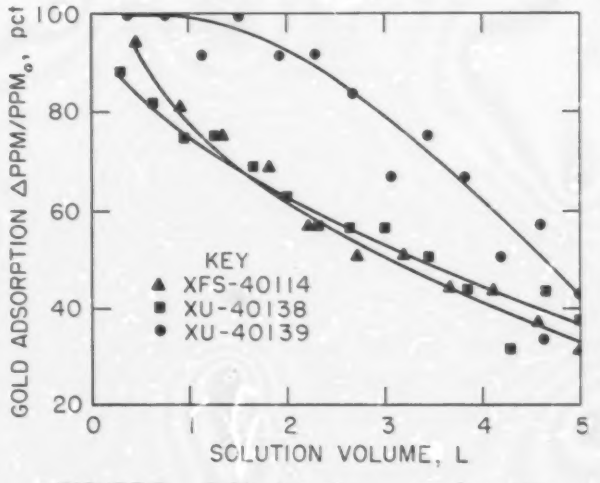

FIGURE 7. - Gold adsorption curves for resins XFS-40114, XU-40138, and XU-40139 with actual leach solution.

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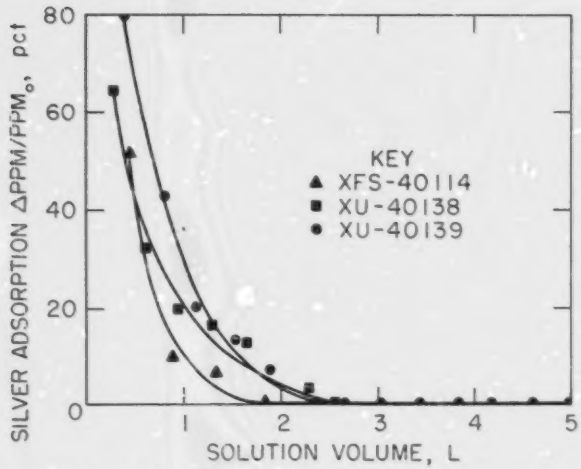

FIGURE 8. - Silver adsorption curves for resins XFS-40114, XU-40138, and XU-40139 with actual leach solution.

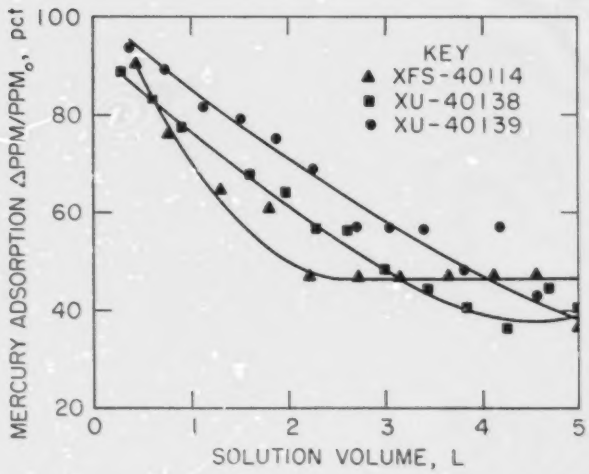

FIGURE 9. - Mercury adsorption curves for resins XFS-40114, XU-40138, and XU-40139 with actual leach solution.

These three resins (XFS-40114, XU-40138, and XU-40139) were generally selective for gold and mercury, with minimal silver and other base metals being adsorbed. The stronger the attraction a resin had for gold and mercury, the less selective it was and the poorer the elution with NaOH. The exchange resin XU-40138 appeared to show the best loading and eluting characteristics. During this experiment, XU-40138 loaded to about 140 tr oz/st Au and produced an eluant containing an average of 12.4 ppm Au. By comparison, XU-40139 and XFS-40114 loaded 134 and 97 tr oz/st Au, respectively, and eluted average Au concentrations of 1.7 and 3.9 ppm, respectively. The weak-base resin XU-40138 may have a commercial application if cyclic loading-elution tests are successful.

SUMMARY AND CONCLUSIONS

Strong-base anion-exchange resins were loaded with gold, silver, and mercury, then sequentially eluted with various eluants. Sequential elution of Amberlite IRA-430, for example, eluted 100 pct of the mercury with 2N H_2SO_4, 100 pct of the silver with 200 g/L NaCl in 1N HCl, and all of the remaining gold with 0.75 pct NaClO in 150 g/L NaCl plus 5 g/L NaOH. Depending on the strong-base resin examined, this elution scheme allowed little contamination between the mercury and the precious metals.

In addition to strong-base resins, weak-base resins were investigated for possible applications in the caustic-cyanide systems of the gold industry. None of the commercial weak-base resins tested was suitable for a caustic-cyanide system; however, three experimental resins have possible application because of their effectiveness in the pH range of 10 to 12. When using a mill leach solution, these resins adsorbed the gold and mercury with only minimal silver being adsorbed.

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STAGED HEAP LEACHING-DIRECT ELECTROWINNING

By C. H. Elges[1] and M. D. Wroblewski[2]

ABSTRACT

The Bureau of Mines is conducting research to develop a staged, agglomeration heap leaching system employing direct electrowinning of dissolved precious metals from the pregnant leaching solution. This paper describes bench-scale research the Bureau conducted to develop such a system and an efficient electrowinning cell.

The Bureau demonstrated through leaching simulations that pregnant solutions suitable for direct electrowinning can be generated by staged heap leaching. The Bureau also demonstrated that improved mass transfer (IMT) cells can recover precious metals from low-grade pregnant solutions generated by cyanide heap leaching. This research indicates that staged heap leaching-direct electrowinning is a promising technique for recovering precious metals from low-grade resources.

INTRODUCTION

Heap leaching has been used to recover gold and silver from low-grade ores since the early 1970's, and numerous operations in the Western United States are presently using heap leaching to produce precious metals (1-3).[3] One stimulus for the rapid increase in the number of commercial operations has been the dramatic and sustained increase in the price of gold. Another stimulus has been a succession of improvements in the practice of heap leaching that has made possible the treatment of increasingly difficult ores.

Current heap leaching practice for precious metals includes sprinkling dilute alkaline NaCN solution on heaps of crushed material, which may have been agglomerated with cement or lime (4-6), and allowing the solution to percolate through the heap. The effluent is collected and passed through activated carbon beds that adsorb the precious metals. For ores in which the silver content is high relative to the gold content, Merrill-Crowe zinc precipitation may be favorable; this technique avoids the large carbon inventories required to adsorb the larger quantity of silver. When carbon is used, the precious metals are removed by stripping at elevated temperature with a strong caustic-cyanide solution, often with the addition of methyl or ethyl alcohol (7). Gold and silver are recovered from the stripping solution by electrowinning onto a steel wool cathode and are then fire-refined to produce dore metal.

The carbon adsorption-desorption step is an efficient way to concentrate the typically dilute gold solutions (about 1 mg/L) from heap leaching. However, because the carbon is usually acid-washed and must be thermally regenerated before reuse, the carbon adsorption-desorption step can add significantly to the operating and capital costs of a heap leaching operation. In marginal cases, this step may make an operation uneconomical. In addition, there are precious metals losses associated with loss of carbon from the system. For these reasons, it is desirable to eliminate the carbon adsorption-desorption step and directly electrowin the gold from the heap effluent.

For staged heap leaching-direct electrowinning to be efficient, the precious metals concentration of the pregnant solution generated during leaching must be

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[3]Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

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higher than that obtained by conventional heap leaching, and the solutions may have to be fortified with electrolyte. The precious metals concentration of the pregnant solution can be increased by (1) leaching with smaller volumes of solution, (2) agglomeration pretreatment with cyanide solution (which starts the leaching process during the curing period), and (3) cycling the leaching solution through more than one heap in a staged manner. The resultant pregnant solution is passed directly through an electrowinning circuit. The barren solution from electrowinning is recycled to the leaching circuit.

For direct electrowinning of precious metals to be commercially feasible, it is necessary to obtain suitable recoveries in electrolytic cells of reasonable size and at ambient temperature, because heating large volumes of solution is costly. This objective is made more difficult because the concentration of precious metals in heap leaching solutions is very low. A typical heap leaching pregnant solution contains 0.5 to 2.0 mg/L Au, compared to 50 to 1,000 mg/L Au in carbon stripping solutions from which gold is conventionally electrowon. The requirements for direct electrowinning are (1) precious metals electrowinning cells that operate more efficiently at ambient temperature than those currently in use and (2) a method for conducting heap leaching operations that maximizes the precious metals content. The Bureau is currently investigating direct electrowinning of gold and silver from heap leaching solutions and has developed electrolytic cells with IMT characteristics. Countercurrent staged heap leaching techniques are being improved in order to increase the concentration of precious metals in the heap effluent.

DIRECT ELECTROWINNING

CELL DESIGN

The Bureau's original IMT cell design is similar to that of the Zadra cell, which has been the industry standard for gold electrowinning for many years (8). The Zadra cell (fig. 1) features three concentric circular containers. The inner container, which serves as the cathode compartment, is a perforated insulator that contains a central feed tube, current distributor, and steel wool, onto which precious metals are deposited. The anode, a circular stainless steel screen, is outside the cathode in the second container. Pregnant solution enters through the central feed tube and flows upward and outward through the steel wool. Zadra-type cells have been used to electrowin precious metals from stripping solutions at temperatures of 70° to 85° C. However, several disadvantages of the Zadra design are that solution flow is unevenly distributed, "effective" electrode spacing is excessive,[4] and cell volume is utilized inefficiently.

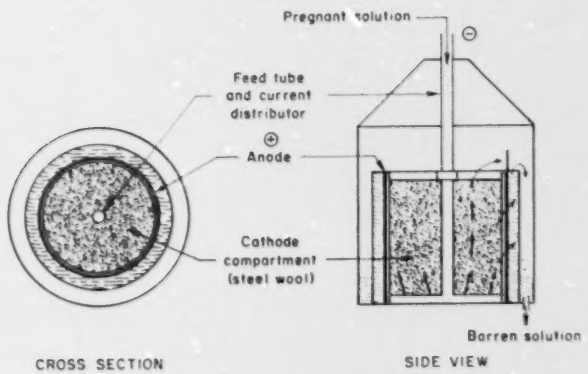

FIGURE 1. - Zadra cell design.

The circular IMT cell (fig. 2) was designed to overcome the problems of the Zadra cell by providing uniform solution flow across and through the cathodic steel wool. The solution distribution tube is stainless steel and serves as a second anode, which decreases the effective electrode spacing. To increase the cell efficiency, provision was made for rapid internal solution circulation. Although the mean residence time is unaffected by this internal circulation, the

[4]The physical properties of the pervious steel wool cathode preclude exact measurement of electrode spacing.

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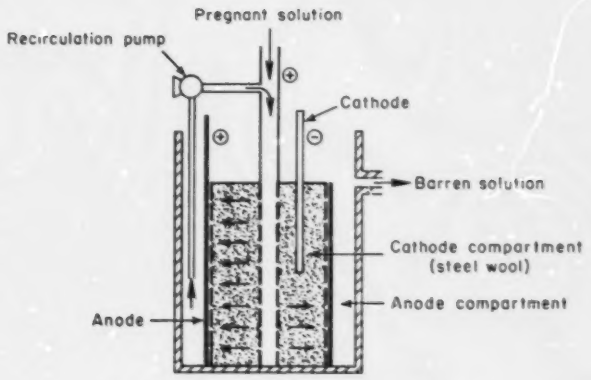

FIGURE 2. - Design of large IMT cell.

highly turbulent flow results in a thinner electrode boundary layer, decreases concentration polarization, and increases metal deposition rates up to 200 pct. Internal circulation flow rates were 10 to 25 times the pregnant solution feed rate. The circular cell was built in several sizes, ranging from 55 to 888 cm^3 (cathode volume).

The data presented in this paper were generated using circular IMT cells, although current research efforts are concentrated on a rectangular IMT cell. The rectangular cell is similar in appearance to "breadbasket" types currently in use. It should scale up easily while retaining the favorable operating characteristics of the circular cell.

ELECTROWINNING TESTS

Direct electrowinning tests were made using small (55 cm^3 cathode volume) and large (888 cm^3) circular IMT cells. The cells were operated at ambient temperature (20° to 25° C) with voltage, amperage, feed rate, internal circulation rate, NaOH concentration, and precious metals concentration as variables. Small-cell tests were performed by pumping solution from a reservoir through the cell numerous times, using various flow rates and operating times. Large-cell tests were made by passing feed solution through the cell once, but with internal circulation of the solution.

For comparison, direct electrowinning tests were made using small (67 cm^3 cathode volume) and large (888 cm^3) Zadra

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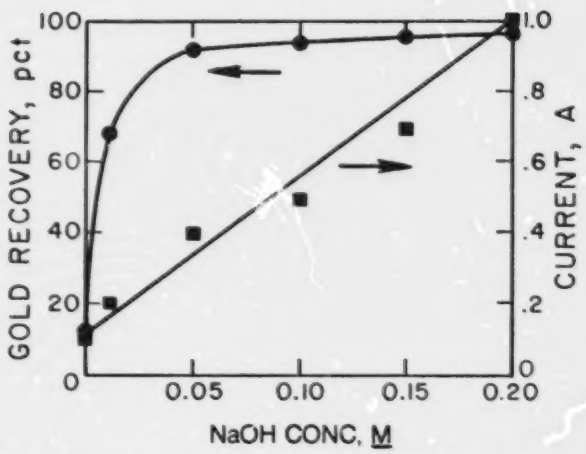

FIGURE 3. - Recovery of gold with increasing NaOH concentration. (Cell operated at 3 V and feed rate of 72 mL/min.)

cells. The cells were operated at 3 V and ambient temperature (20° to 25° C). Retention time in the cells was varied.

RESULTS AND DISCUSSION

Operating data and results are given for the small circular IMT cell in table 1 and for the large circular IMT cell in tables 2 and 3. The results show that flow rate and NaOH concentration are important parameters. Pregnant solutions from heap leaching are unsuitable as cell electrolytes unless they are fortified with electrolyte. Figure 3 shows the increase in gold recovery with the addition of NaOH to 0.05M (4 lb/st of solution) in the large IMT cell.

Although NaOH was the most effective additive for fortifying the electrolyte, other salts were investigated. Na_2CO_3 functioned well, but was not as effective on a molar basis. Two salts of strong acids, Na_2SO_4 and $NaNO_3$, were also investigated but caused severe corrosion of the stainless steel anodes.

The effects of the circulation flow rate on gold and silver recovery in the small IMT cell are shown in figure 4. Recovery of both metals increased markedly with increased flow rates up to approximately 250 mL/min and then decreased.

The effects of the internal circulation flow and feed rates on gold and silver

TABLE 1. - Performance of small IMT cell[1]

Current, A	Operating time, h	Flow rate, mL/min	NaOH conc, M	Recovery, pct		Deposition rate, mg/min	
				Au	Ag	Au	Ag
0.07	1.0	30	0.10	54	73	0.3	0.6
.08	1.0	75	.10	74	81	.5	.7
.08	1.0	150	.10	90	96	.6	.8
.09	1.0	240	.10	92	100	.8	1.0
.09	1.0	420	.10	84	99	.6	.9
.09	1.5	250	.10	97	100	.5	.7
.03	2.0	250	.01	43	26	.2	.1
.03	2.0	250	.02	46	31	.2	.1
.06	2.0	250	.05	61	78	.2	.4
.08	2.0	250	.10	84	91	.3	.4
.09	2.0	250	.15	92	92	.3	.4
.12	2.0	250	.20	96	96	.3	.5

[1]Cell operated at 3 V. Pregnant synthetic solutions contained approximately 40 mg/L Au and 50 mg/L Ag. Cathode packing density, 0.018 g/cm^3 (1 g steel wool).

TABLE 2. - Performance of large IMT cell showing effects of internal circulation flow rate and feed rate[1]

Current, A	Retention time, min	Internal circulation flow rate, L/min	Feed rate, mL/min	Recovery, pct		Deposition rate, mg/min	
				Au	Ag	Au	Ag
0.6	8.6	0	250	43	56	4.5	7.0
.7	8.6	.5	250	60	70	6.3	8.8
.7	8.6	1.0	250	67	78	6.5	10.3
.8	8.6	1.5	250	73	85	6.8	10.2
.8	8.6	2.0	250	75	81	7.4	9.1
.8	21.5	2.0	100	86	91	3.7	6.4
.8	4.3	2.0	500	51	63	8.1	16.0

[1]Cell operated at 3 V with 0.1M NaOH. Pregnant synthetic solutions contained approximately 40 mg/L Au and 50 mg/L Ag. Cathode packing density, 0.018 g/cm^3 (16 g steel wool).

TABLE 3. - Performance of large IMT cell showing effects of cell voltage and NaOH concentration[1]

Potential, V	Current, A	NaOH conc, M	pH	Au recovery, pct	Deposition rate, mg/min	Current efficiency, pct
1.5	~0	0.05	12.75	0	0	0
2.0	.1	.05	12.75	39	1.8	23.4
2.5	.3	.05	12.75	64	2.0	12.9
3.0	.4	.05	12.75	90	2.8	14.8
3.5	.6	.05	12.75	95	2.9	9.8
4.0	.8	.05	12.75	97	3.0	7.6
3.0	.1	~0	9.35	12	.4	7.3
3.0	.2	.01	10.45	68	2.1	21.0
3.0	.4	.05	12.75	90	2.8	14.8
3.0	.5	.10	13.05	94	2.9	11.5
3.0	.7	.15	13.13	96	3.0	8.5
3.0	1.0	.20	13.40	97	3.0	6.3

[1]All tests used a retention time of 12.3 min, a feed rate of 72 mL/min, and an internal circulation flow rate of 2 L/min. Pregnant solutions contained 43 mg/L Au and 1 mg/L Ag. Cathode packing density, 0.018 g/cm^3.

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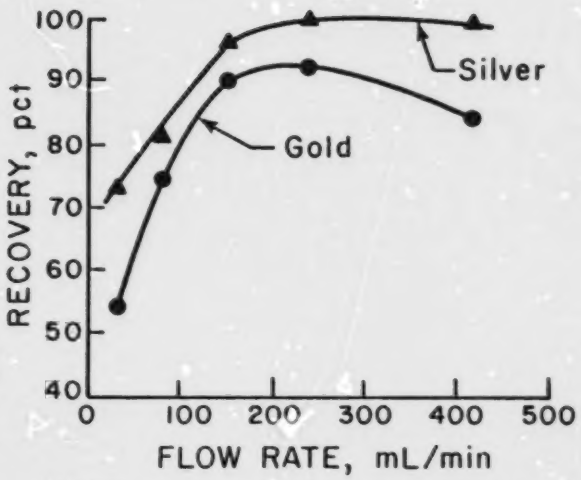

FIGURE 4. - Recovery of gold and silver with increasing circulation flow rate after 1 h of operating time. (0.01M NaOH.)

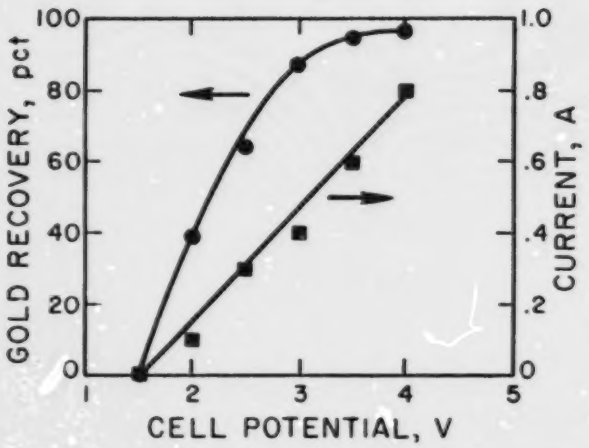

FIGURE 5. - Recovery of gold with increasing cell potential. (0.05M NaOH; feed rate, 72 mL/min; internal circulation flow rate, 2 L/min; retention time, 30 min.)

recovery in the large IMT cell are shown in table 2. Gold and silver recovery and deposition rates increased as the internal circulation flow rate increased. When the feed rate was increased, gold and silver recovery decreased, but the deposition rates increased. The data show that silver is more easily electrowon than gold; consequently, adjustment of electrowinning parameters to achieve the best gold recovery will ensure good silver recovery.

The effects of decreasing gold concentration in the feed to the small IMT cell are shown in table 4. Deposition rates decreased with decreasing gold concentration, and the current efficiency decreased to <1 pct when the gold concentration in the pregnant solution was less than 7 mg/L.

The effects of cell voltage on gold recovery and cell current in the large IMT cell are shown in figure 5. Current varied directly with applied voltage, and gold recovery increased at greater cell currents. Figure 6 shows that while gold deposition rates increased with increased cell potential, current efficiency decreased sharply. When the cell potential was increased above 2 V, a greater proportion of the current was used in the decomposition of water as opposed to the deposition of gold.

Table 5, which compares the operation of large Zadra and IMT cells, shows that gold and silver recovery, current

TABLE 4. - Performance of small IMT cell with decreasing gold concentration in feed solution[1]

Au in pregnant sol, mg/L	Au recovered in 1 h of operating time, pct	Deposition rate, mg/min	Current efficiency, pct
48.....	92	0.72	9.6
37.....	93	.60	8.6
10.....	91	.28	2.3
7.4.....	84	.11	1.5
3.8.....	82	.07	.71
2.1.....	85	.03	.50
1.1.....	81	.015	.20

[1]Cell operated at 3 V, with a flow rate of 240 mL/min, a retention time of 3.3 min, an NaOH concentration of 0.10M, and a cathode packing density of 0.018 g/cm^3.

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TABLE 5. - Recovery of gold and silver in large electrolytic cells[1]

Feed rate, mL/min	Current, A	Synthetic pregnant solution, mg		Recovery, mg		Current efficiency, pct		Deposition rate, mg/min	
		Au	Ag	Au	Ag	Au	Ag	Au	Ag
ZADRA CELL									
100	0.60	592	720	290	403	2.5	6.3	1.8	2.5
250	.75	656	880	112	336	1.9	10.5	1.8	5.3
500	.75	640	896	64	208	2.2	12.9	2.0	6.5
IMT CELL									
100	0.95	688	1,136	594	1,030	3.2	10.1	3.7	6.4
250	.95	608	816	440	629	5.9	15.4	6.9	9.8
500	.97	512	816	261	512	6.9	24.6	8.2	16.0

[1]Both cells were operated at ambient temperature, at 3 V, with a cathode packing density of 0.018 g/cm^3, a feed volume of 16 L, and 0.1M NaOH. The IMT cell had an internal circulation flow rate of 2 L/min. Recovery based on 1 pass through cell.

efficiency, and deposition rate, were all substantially higher for the IMT cell than for the Zadra cell, especially at higher feed rates.

STAGED HEAP LEACHING

HEAP PREPARATION AND LEACHING CYCLE

Staged heap leaching was developed to produce pregnant solutions with the highest possible gold concentration. Figure 7 is a schematic of staged heap leaching operated in conjunction with direct electrowinning. Using this scheme, several heaps are leached countercurrently before the pregnant solution is routed to electrowinning. The ore in the heaps is agglomerated with cement and a strong NaCN solution. The leaching action of NaCN starts during the curing period and may be almost finished by the time the heap is constructed. The dissolved Au and Ag can be removed from the heap by repeated washing with a small volume of water or dilute NaCN solution. Leaching solution is applied intermittently because a "pulsed" flooding cycle resulted in higher precious metals extraction and used less leachant.

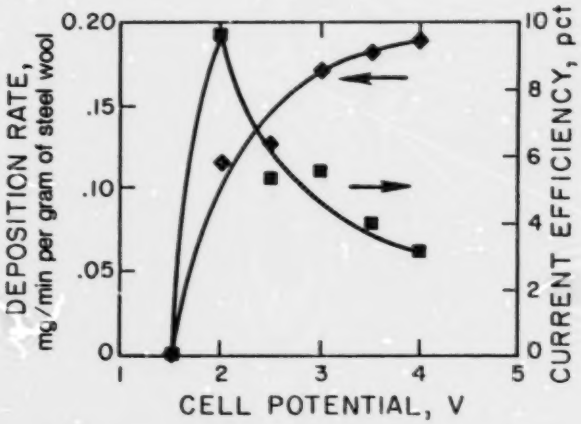

FIGURE 6. - Effect of cell potential on deposition rate and current efficiency. (0.05M NaOH; feed rate, 72 mL/min; internal circulation flow rate, 2 L/min, retention time 30 min.)

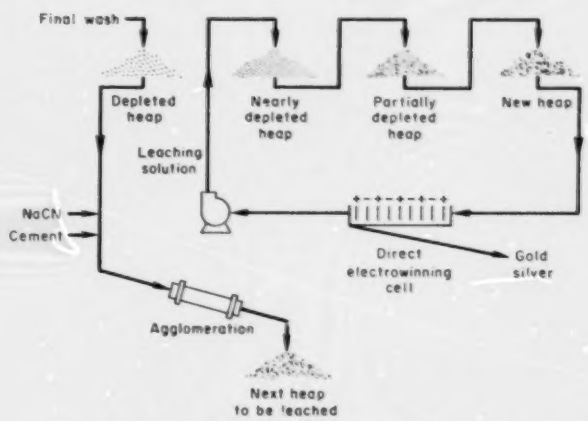

FIGURE 7. - Staged heap leaching-direct electrowinning.

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After leaching of a heap is completed, a thorough washing cycle is conducted to recover additional values. The wash water is fortified with NaCN and used to agglomerate a new charge of ore for heap leaching.

LABORATORY TESTS

To conduct staged heap leaching-direct electrowinning experiments in the laboratory, 22.7-kg (50-lb) charges of ore were agglomerated and percolation leached in acrylic columns 5-ft high by 5.5 in ID. Agglomeration was accomplished with a disk pelletizer in which the 22.7-kg ore charges were combined with 227 g portland cement (20 lb/st ore) and 2.5 L of 0.10M NaCN-0.05M NaOH solution (9.8 and 4.0 lb/st solution, respectively). The agglomerated ore was placed in columns and aged for at least 24 h. A small IMT cell containing 1 g of steel wool and operated at 3 V and a flow rate of 250 mL/min was used to recover gold and silver from solution.

Each test series used five columns, each containing a 22.7-kg charge of agglomerated ore. As shown in figure 8, the laboratory procedure was to bring columns on-line in stages, such that steady-state operation could be approximated by the completion of the test series. In stage 1, 1 L of 0.05M NaOH (4 lb/st solution) was used to start the leaching process; after progressing to stage 3, there were three 1-L batches of leachant in the system. Electrowinning was conducted after each cycle of leaching, and the barren cell electrolyte was recycled to the next stage of leaching. Additions of NaOH, when required, were made prior to electrowinning, while solution volumes were adjusted prior to each leaching step. Upon completion of leaching of columns 1 and 2, these columns were subjected to wash cycles using 2.5-L quantities of water. The wash waters were then fortified with NaCN and NaOH and used to agglomerate the ore charges to columns 4 and 5, respectively.

Objectives throughout the leaching-electrowinning sequence were to obtain maximum precious metals recovery while maintaining the greatest possible precious metals tenor in the pregnant leach solutions. Pregnant solution analyses are ideally based upon the average of the pregnant leaching solutions produced during stage 5. Precious metals recoveries are ideally based upon the tails analysis of column 3 after completion of stage 5. A total of 25 to 30 cycles of leaching-electrowinning were employed per test series.

RESULTS AND DISCUSSION

Results of staged heap leaching-direct electrowinning tests on four ores of differing grade and mineralogy are given in table 6. The gold concentration of the pregnant solutions produced was a function of the ore grade. For the ores

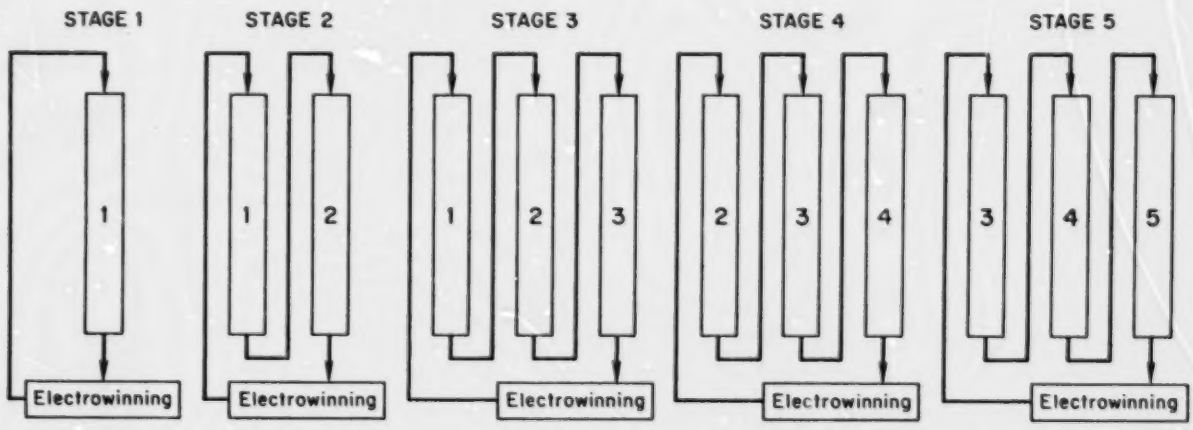

FIGURE 8. - Laboratory-scale staged leaching of agglomerated ores. (Numbers identify leaching columns.)

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TABLE 6. - Recovery of gold by staged heap leaching-direct electrowinning

	Test			
	1	2	3	4
Ore grade.....ppm Au..	9.3	4.8	2.1	1.1
Gold recovery from ore, pct:				
Staged heap leaching.....	87	91	83	73
Conventional leaching.....	86	99	83	74
Average content of pregnant solution.....mg/L..	32.5	26.7	12.3	4.4
NaOH used.....kg/mt ore..	0.43	0.49	0.51	0.41
Current efficiency.....pct..	7.3	2.0	1.5	0.7
Gold recovery, electrowinning, pct:				
Batch (average).....	89	90	91	90
Overall.....	98	99	99	99

tested, the pregnant solutions generated in each case were at least an order of magnitude higher in precious metals values than would be typical of solutions generated using conventional leaching practice. The increases in precious metals tenor were achieved in three of the four tests with no measurable sacrifice in precious metals recovery. Overall recovery of precious metals from solution by electrowinning was more than 98 pct in all cases.

Impurity buildup was not a problem during the staged heap leaching-direct electrowinning tests. Impurities were closely monitored during test 4, which was conducted on gold ore containing 1.1 g/mt Au (0.035 tr oz/st Au). Impurities that accumulated in the pregnant feed to the IMT cell were silicon (4 ppm), mercury (10 ppm), calcium (20 ppm), copper (21 ppm), and zinc (200 ppm). Only the mercury codeposited with the precious metals.

CONCLUSIONS

The research demonstrated that IMT cells can recover precious metals from low-grade pregnant solutions generated by cyanide heap leaching. Efficient operation at ambient temperature makes the IMT cell suitable for direct electrowinning. Major differences in comparison with the standard Zadra cell are the rapid recirculation of solution within the cell, better control of solution flow streams, and ambient temperature operation.

Simulated staged heap leaching demonstrated that suitable pregnant solutions for direct electrowinning can be generated. The buildup of impurities in the recycled leachant and/or electrolyte did not affect the electrowinning step in the number of cycles studied. Staged percolation leaching-direct electrowinning shows considerable promise as a technique for recovering precious metals from low-grade resources.

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MERCURY PRECIPITATION DURING CYANIDE LEACHING OF GOLD ORES

By Richard G. Sandberg[1]

ABSTRACT

Many gold-bearing ores throughout the Western United States contain small quantities of mercury. During cyanidation, 10 to 40 pct of the mercury is extracted along with the precious metals. The presence of mercury decreases gold loading and increases stripping time on activated carbon, complicates fire refining of the gold cathodes, and creates a possible health hazard. In the investigation described in this paper, the Bureau of Mines examined several methods for removing mercury from gold-silver cyanide leach slurries.

CaS addition to cyanide leach slurries or to a laboratory ball mill containing NaCN and lime reduced mercury dissolution to < 0.5 pct. Mercury loading on activated carbon was reduced to < 0.2 pct. Gold loading on activated carbon was affected very little by sulfide addition; however, silver loading was reduced to 0 to 6 pct, as opposed to the typical values of 90 to 100 pct of the silver and none of the mercury being adsorbed on the carbon.

Preliminary testing in a mill operation using NaHS showed that mercury precipitation was nearly complete at the point of addition; however, as with Na_2S, 30 to 50 pct of the precipitated HgS redissolved with time.

INTRODUCTION

Mercury contamination has been a problem in the recovery of gold and silver from many western deposits, which may contain as much as 20 ppm Hg. During the cyanide leaching process, 10 to 40 pct of the mercury is normally solubilized along with gold and silver. The mercury must be recovered or precipitated so that it does not present a health hazard during electrolysis, smelting of the cathodes, and regeneration of activated carbon. Some gold mill operations recover mercury by retorting the cathodes prior to smelting (1-2)[2] or autoclaving the ore to extract minimal mercury (3).

In an effort to reduce mercury solubilization, the Bureau of Mines conducted bench-scale leaching tests with an ore containing 0.08 tr oz/st Au, 0.06 tr oz/st Ag, and 17 ppm Hg (4). Leaching was accomplished with cyanide in an air-agitated Pachuca-type vessel. Mercury extraction was decreased from 40 to 10 pct by (1) decreasing NaCN concentration from 20 to 0.34 lb per short ton of solution, (2) decreasing the pH from 11.5 to 11, and (3) increasing particle size from minus 270 mesh to minus 10 plus 48 mesh. Although mercury extraction was reduced, it was not eliminated.

The remaining soluble mercury can be precipitated with sulfides as shown by the chemical reaction

$$Hg(CN)_4^{2-} + MS \rightarrow HgS + M^{2+} + 4CN^-.$$

Calcium, sodium, silver, iron, and zinc sulfides have been used to precipitate mercury from $Au(CN)_3$ solutions (4-5). Addition of Ag_2S would tie up considerable silver, and excess Ag_2S would have to be recovered. FeS is undesirable because of cyanide loss due to ferrocyanide formation. Calcium and sodium sulfides are effective in precipitating mercury and are not harmful to gold recovery. This paper reports on a number of tests in which calcium and sodium sulfides were used to remove mercury from gold and gold-silver cyanide leach slurries.

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[2]Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

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MERCURY PRECIPITATION FROM SLURRY

Gold ore containing 17 ppm Hg was leached with solutions containing 0.34 or 6 lb NaCN per short ton of solution and enough lime to give a pH of 11, then contacted with Na_2S. The results of these tests are shown in figure 1. Increasing Na_2S lowered mercury extraction when low concentrations of cyanide (0.34 lb/st NaCN) were used. However, when high concentrations of cyanide (6 lb/st NaCN) were present, increasing the sulfide concentration in the solution increased mercury extraction. This was probably due to the formation of a soluble HgS_2^{2-} complex (6). Because of this complex formation, high concentrations of Na_2S have been used to extract mercury from concentrates (7). However, care must be taken to control the amount of sulfide added, since the addition of too much Na_2S may increase mercury extraction instead of precipitating mercury as desired.

To determine the effects of Na_2S concentration and time on mercury precipitation (as HgS), additional tests were conducted. Solutions containing 0.34 lb/st NaCN were contacted with gold ore for 24 h to extract 12 pct of the mercury; then Na_2S was added. Using ore containing only 0.02 lb/st Na_2S, 79.9 pct of the solubilized mercury was precipitated. However, within 0.5 h, the precipitated mercury began to redissolve, and 4 h later, nearly 30 pct of it had redissolved.

Because the HgS redissolved, CaS was investigated as an alternative. In one test, a cyanide solution containing 0.34 lb/st NaCN (with no sulfides) extracted 12 pct of the mercury in 24 h. After adding only 0.02 lb/st CaS to this solution, 99.8 pct of the mercury was precipitated in only 0.5 h, and 7 h later, only 7 pct of the precipitated HgS had redissolved. A followup test, using 0.09 lb/st CaS, precipitated 100 pct of the soluble mercury; after 24 h, < 0.01 pct of the HgS had redissolved.

A comparison between HgS redissolution using Na_2S and CaS is shown in figure 2. About 10 times more HgS redissolved with Na_2S than with CaS after 4 h. This may be due to the formation of the soluble Na_2HgS_2 complex (6). CaS is less likely to form this type of complex because of its insolubility.

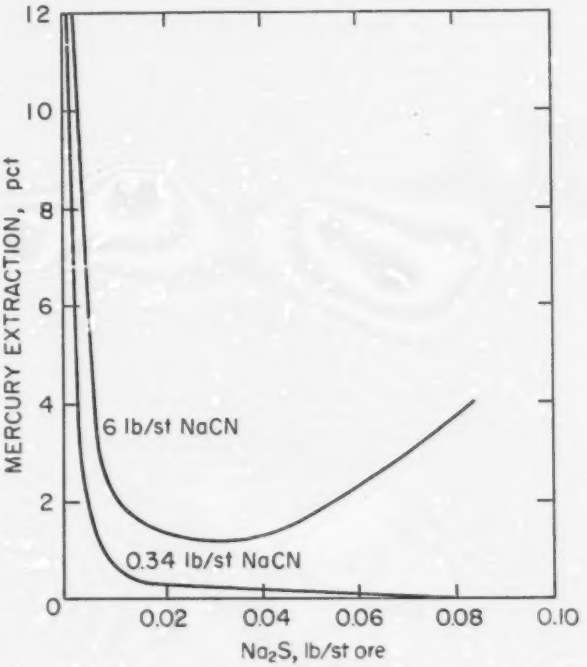

FIGURE 1. - Effect of Na_2S and NaCN on mercury extraction.

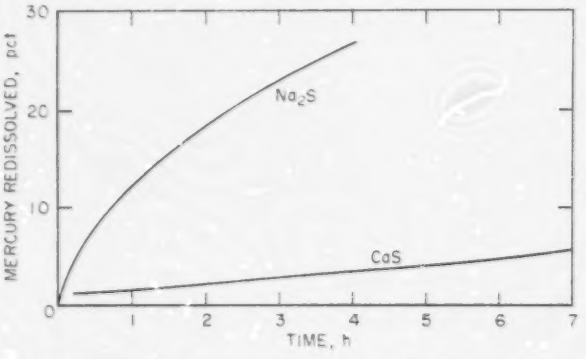

FIGURE 2. - Effect of time on sulfide precipitation of mercury.

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MERCURY PRECIPITATION AND CARBON ADSORPTION

SIMULATED CARBON-IN-PULP

Because most gold operations use activated carbon to recover precious metals, tests were conducted to determine the effect of sulfide addition on carbon adsorption of gold and mercury in a laboratory carbon-in-pulp (CIP) circuit. Five hundred grams of dry ground gold ore was leached with 870 mL of leach solution containing 0.34 lb/st NaCN and enough lime to give a pH of 11. The slurry was rolled for 24 h, then various amounts of CaS were added and rolling was continued for 1 h. Following HgS precipitation, 18 g/L activated carbon was added and mixed for 1 h. The carbon was screened from the slurry, and the slurry was contacted with fresh carbon a second and third time.

Results of these tests are listed in table 1. Gold and silver adsorption on carbon without prior CaS addition was nearly 100 pct after the first stage, while only 61 pct of the soluble mercury adsorbed. Additional adsorption stages recovered 9 pct more of the mercury. With 0.023 lb/st CaS, mercury adsorption was reduced to about 5 pct, without decreasing gold and silver adsorption; however, with 0.047 lb/st CaS addition, there was a slight decrease in silver adsorption and mercury adsorption decreased to 0.9 pct.

TABLE 1. - Carbon-in-pulp adsorption with CaS precipitation, percent[1]

Carbon stage	Au	Ag	Hg
0 lb/st CaS:			
1.....	99	97	61
2.....	1	3	7
3.....	0	0	2
0.023 lb/st CaS:			
1.....	99	96	4.7
2.....	1	4	.4
3.....	0	0	.3
0.047 lb/st CaS:			
1.....	99	95	.37
2.....	.6	4.1	.31
3.....	.1	.5	.20

[1]Percent of soluble metal (prior to CaS addition) adsorbed on carbon.

LABORATORY GRINDING CIRCUIT

Several gold operations add NaCN and lime to the grinding circuit to extract gold and silver. Because some of the mercury is also extracted at the same time, tests were conducted to determine if addition of CaS to the ball mill would prevent mercury extraction and how it would affect gold, silver, and mercury loading on carbon. The following were added to a laboratory ball mill and ground for 45 min: 1,000 g of minus 10-mesh ore, 0.5 lb/st NaCN, 1,000 mL H_2O, enough lime to give a pH of 11, and varying amounts of CaS. Each resulting slurry was washed into a 9-L bottle with 2,000 mL H_2O and mixed. Gold and silver were removed from the slurry by adsorption on activated carbon in three stages. One gram of fresh carbon was used in each stage. The total carbon contact time was 24 h.

The results of these tests are given in table 2. Mercury extraction and adsorption on carbon were decreased from 15 to 0.4 pct and from 5.5 to 0.17 pct, respectively, by increasing the amount of CaS from 0.012 to 0.096 lb/st. Gold extraction decreased slightly, but gold loading on carbon was essentially unaffected. Silver extraction was unaffected, but silver adsorption decreased. Both gold and silver adsorption on carbon was lower than in previous sulfide precipitation tests. This was because much less carbon was used (0.33 g/L) than is normally used (18 g/L). Decreasing the carbon

TABLE 2. - Effect of CaS addition during grinding on mercury, gold, and silver extraction and adsorption, percent

CaS, lb/st	Extraction[1]			Adsorption on carbon[2]		
	Au	Ag	Hg	Au	Ag	Hg
0.012.....	99	86	15	91	71	5.5
.024.....	94	98	1.5	87	74	.55
.048.....	94	98	2	88	67	.40
.096.....	95	98	1.4	89	64	.17

[1]Total extraction including grinding (45 min) and carbon addition (24 h).
[2]24 h contact with carbon.

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concentration made it possible to analyze for the small amount of mercury adsorbed on the carbon.

GOLD-SILVER ORES

Because silver was precipitated during mercury precipitation with CaS, additional tests were conducted. The purpose of these tests was to determine the effects of adding CaS and to find a way to prevent silver precipitation. The ores used in this study are listed in table 3.

TABLE 3. - Analyses of gold-silver ores

Ore	Hg, ppm	Ag, tr oz/st	Au, tr oz/st	Cu, pct
Carline....	16	2.52	0.098	NAp
Cortez.....	9	.17	.013	NAp
Silver Reef	3	10.1	.01	0.8

NAp Not applicable.

The ores were leached with 1 lb/st NaCN for 24 h; then CaS was added and mixed in for 1 h. Following mercury precipitation, the slurry was contacted with activated carbon for 1 h. The test results are listed in table 4. Without CaS addition, gold, silver, and mercury adsorption values were all 100 pct; however, with CaS addition, both the silver and mercury adsorption values were greatly reduced for all ores except the Silver Reef ore.

Tests were conducted to determine why silver was not precipitated from the Silver Reef slurry during mercury precipitation. Close analysis of the Silver Reef pregnant leach solution showed that it contained 170 ppm Cu. To eliminate silver loss during mercury precipitation, various amounts of CuCN were added to a pregnant leach solution containing 1.5 ppm Au, 3 ppm Ag, and 0.76 ppm Hg prior to the addition of 0.1 lb/st CaS. The results given in figure 3 show that the addition of 160 ppm Cu eliminated silver loss; but the copper addition did not affect precipitation of the mercury.

Additional tests were conducted as described in table 4, except that 235 ppm Cu was added prior to mercury precipitation. The results listed in table 5 show that silver recovery was greatly increased. Carlin and Cortez silver adsorption was increased from 0 to 80 pct and 6 to 91 pct, respectively. Mercury adsorption was zero for all ores.

TABLE 4. - Adsorption on carbon in simulated three-stage carbon-in-pulp operation with CaS precipitation, percent[1]

Carbon stage	Au	Ag	Hg
CARLIN ORE			
0 lb/st CaS:			
1.....	90	91	100
2.....	9	9	0
3.....	1	0	0
0.10 lb/st CaS:			
1.....	50	0	8.1
2.....	41	0	0
3.....	9	0	0
CORTEZ ORE			
0 lb/st CaS:			
1.....	57	75	100
2.....	30	25	0
3.....	13	0	0
0.10 lb/st CaS:			
1.....	64	6	2
2.....	25	0	0
3.....	11	0	0
SILVER REEF ORE			
0 lb/st CaS:			
1.....	100	99	100
2.....	0	1	0
3.....	0	0	0
0.10 lb/st CaS:			
1.....	100	51	0
2.....	0	25	0
3.....	0	14	0

[1]Percent of soluble metal adsorbed on carbon.

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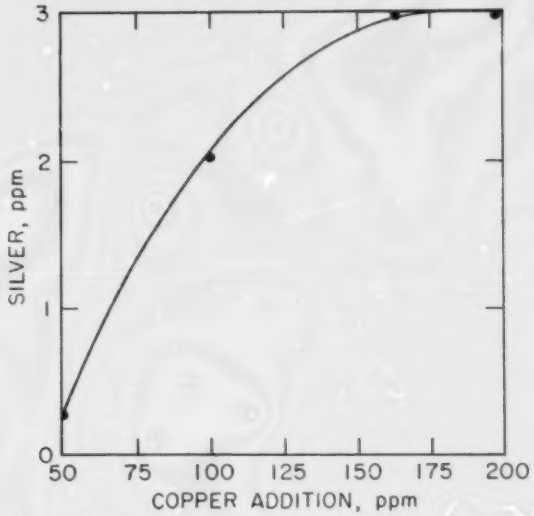

FIGURE 3. - Effect of copper addition on silver precipitation during CaS precipitation of mercury.

TABLE 5. - Effect of copper addition on adsorption on carbon, percent[1]

(CaS addition: 0.1 lb/st)

Carbon stage	Carlin ore			Cortez ore		
	Au	Ag	Hg	Au	Ag	Hg
WITHOUT COPPER ADDITION						
1.....	50	0	8.1	64	6	2
2.....	41	0	0	25	0	0
3.....	9	0	0	11	0	0
WITH 235 mg/L COPPER ADDITION						
1.....	93	60	0	87.5	75	0
2.....	13	13	0	.8	8	0
3.....	7	7	0	.8	8	0

[1]Percent of soluble metal adsorbed on carbon.

MERCURY PRECIPITATION IN A MILL OPERATION

Precipitation of mercury with sulfides is being tested at a northern Nevada mill operation, using a process similar to that illustrated in figure 4. Because CaS was difficult to obtain, sodium hydrogen sulfide (NaHS) is being used instead. A solution containing NaHS is added to the NaCN slurry from the ball mill before the slurry enters the thickener. As shown in table 6 (feed to thickener, days 3 to 6), nearly all of the mercury is precipitated at the point of addition; however, over time, about 30 to 50 pct of this precipitated mercury (HgS) redissolved. This was not unexpected, as NaHS acts similarly to Na_2S, and more NaHS addition points are required to obtain a more complete mercury precipitation. Possible addition points include the final leach tank prior to the CIP tanks and the CIP tanks.

TABLE 6. - Mercury precipitation with NaHS in a mill operation

(Mercury analyses, parts per million[1])

Sampling area	Sampling day					
	1	2	3	4	5	6
Feed to thickener.....	2.5	2.6	0.08	0.02	0.05	0.02
Feed to carbon column (thickener overflow).....	2.6	2.7	.09	.07	.11	.01
Final carbon column.....	2.6	2.8	.16	.03	.09	.02
Feed to leach tanks (thickener underflow).....	2.5	2.8	.68	.47	.83	.19
Feed to carbon in pulp (from leach tank 4).....	2.7	2.9	3.3	1.3	1.8	1.3
Final carbon in pulp (to tailings).....	2.2	2.8	3.2	1.5	1.4	1.2

[1]Mercury remaining in solution.

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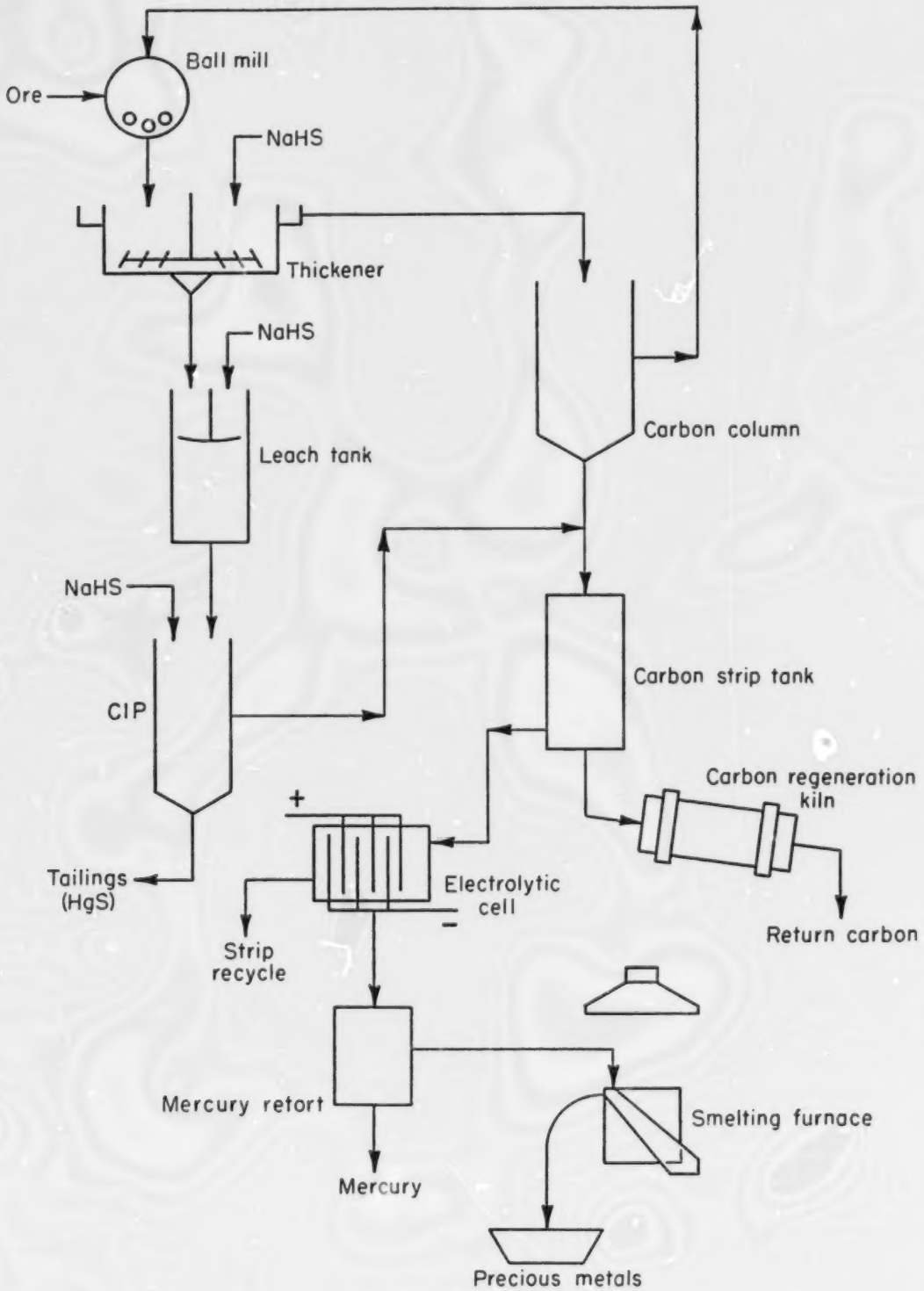

FIGURE 4. - Flowsheet showing NaHS addition points for mercury precipitation in a mill operation.

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CONCLUSIONS

CaS addition to gold-silver cyanide leach slurries or to a laboratory grinding circuit containing NaCN and lime reduced mercury dissolution to < 0.5 pct. Mercury loading on activated carbon was reduced to < 0.2 pct. Gold loading on activated carbon was affected very little by the sulfide addition; however, silver loading appeared to be affected. Additional NaCN-CaS CIP tests with ores containing greater amounts of silver resulted in only 0 to 6 pct of the silver being adsorbed by the carbon rather than the normal 90 to 100 pct. Addition of copper as CuCN, prior to the CaS addition, resulted in 80 to 90 pct of the silver and none of the mercury being adsorbed on the carbon.

Preliminary testing in a mill operation using NaHS showed mercury precipitation was nearly complete at the point of addition; however, as had been found in other tests with Na_2S, 30 to 50 pct of the precipitated HgS redissolved with time.

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CARBONACEOUS GOLD ORES[1]

By B. J. Scheiner[2]

ABSTRACT

The presence of organic material in gold ores interferes with gold extraction by cyanidation. Oxidation of the organic material using chlorine-hypochlorite systems has been shown to render the gold ore amendable to cyanidation. This paper discusses three oxidation procedures that have been investigated by the Bureau of Mines: (1) addition of sodium hypochlorite (NaOCl) to ore pulp, (2) addition of chlorine to ore pulp, and (3) in situ generation of NaOCl by electrolysis of a brine solution used to pulp the ore. Gold extraction was greater than 90 pct when carbonaceous ore was oxidized and then cyanided. Both laboratory and pilot plant results are discussed.

INTRODUCTION

The presence of carbon and organic compounds that inhibit gold recovery from auriferous ores has long plagued cyanide mill operators. Research to develop techniques for testing these ores, which are commonly referred to as carbonaceous ores, was conducted in the early 1920's by the Bureau of Mines (1).[3] Research was continued by the Bureau and others, but as late as 1958, it was indicated that no solution to the carbonaceous problem was at hand (2). After the discovery of carbonaceous gold ores at the Carlin Mine in northeastern Nevada, the Bureau initiated an extensive research program in 1966 to solve the problems associated with extracting gold from these ores.

Research was conducted by the U.S. Geological Survey, the Bureau of Mines, and Newmont Mining Corp., the owners of the Carlin Gold Mine, to characterize the carbonaceous ores found in Nevada (3-5). Early studies indicated that the gold-bearing sedimentary beds were associated with the Roberts Mountain thrust fault system, generally in windows exposing lower plate sedimentary beds of Silurian age. However, later discoveries have shown that the ore association with the Roberts Mountain thrust fault system is just a fortuitous anomaly, since gold has been found in upper plate material outside the Roberts Mountain thrust fault. It has been hypothesized that the gold was redistributed and concentrated in permeable carbonaceous horizons by hydrothermal solutions. Apparently the same solutions replaced much of the silty dolomitic limestone with microcrystalline quartz. Subsequent oxidation induced by shallow meteoric oxygen-bearing waters removed the carbonaceous material from the upper portions of the deposits, thus oxidizing these portions of the deposits. The Carlin Gold Mine property is an example of a deposit that contains both oxidized and carbonaceous gold ores.

CYANIDATION OF CARBONACEOUS ORES

To determine the effect of carbonaceous ores on cyanidation, samples of both oxidized and carbonaceous ore were obtained from various locations in Nevada, including the Carlin Gold Mine, Cortez Gold Mine, and the abandoned Gold Acres pit at Crescent Valley. The gold content of the carbonaceous ores ranged from 0.23 to 0.40 tr oz/st Au, with an organic carbon content ranging from 0.3 to 0.6 wt pct.

Initial experiments involving cyanidation of the carbonaceous ores over a wide

[1]This paper is based upon work done under an agreement between the University of Alabama and the Bureau of Mines.

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[3]Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

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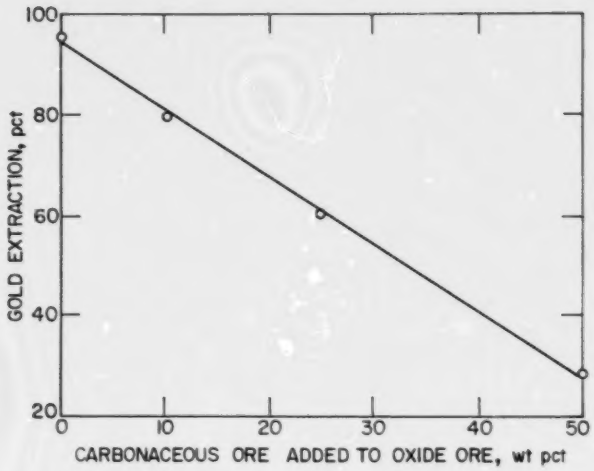

FIGURE 1. - Effect on gold extraction of adding carbonaceous ore to oxide ore.

range of operating conditions showed that only 5 to 32 pct of the gold was amenable to recovery by this conventional technique. The data indicated that cyanide was being consumed, but not excessively. The oxygen content of the leach solution was determined to be favorable for effective cyanidation. Analysis of washed tails detected cyanide, suggesting that $Au(CN)_2^-$ was being adsorbed on carbonaceous components of the ore. The possibility of gold adsorption by carbon was further investigated by contacting 0.1 tr/st of pregnant $Au(CN)_2^-$ solutions with various carbonaceous ores. From 12.5 to 140 tr oz Au was adsorbed per short ton of carbonaceous ore.

To investigate how the addition of carbonaceous material affects the cyanidation of oxidized ores, a series of experiments was conducted in which various amounts of carbonaceous material were added to oxidized ore and the sample cyanided. The results of these experiments are shown in figure 1. Gold extraction decreased linearly as the carbonaceous ore content increased (6-7). Application of the well-known technique of blanking out an activated carbon component by coating it with kerosene or some other petroleum product was shown to be only partially effective, depending on the particular carbonaceous ore being treated. Treatment of the ore with anion-exchange resins or granulated activated carbon during cyanidation in order to actively compete for the $Au(CN)_2^-$ complex generally improved the gold extraction, but the results varied considerably depending on the particular sample being used. This suggested that certain samples of the carbonaceous material contained two different types of carbon that prevented favorable extraction: (1) an activated type of carbon that physically adsorbed the $Au(CN)_2^-$ complex, and (2) a hydrocarbon type that formed a gold compound during deposition that was not attacked by cyanide (6-7).

Gold extraction depended markedly on the basicity of the system, indicating the presence of carboxylic acid groups that saponified in the highly basic ion-exchange system. Isolation of organic compounds in the sample was accomplished by an aqueous NaOH treatment for 2 h, followed by acidification of the liquor and solvent extraction of the dissolved organic compounds into chloroform (3). Infrared spectra of the organic extraction product had major adsorption peaks at 2,900 and 1,700 cm^{-1}, which were characteristic of long-chain carboxylic acids. The neutralization equivalent of this mixture of organic acids was 1,500. Sulfur and nitrogen groups were also found in the organic material. The amounts of organic material that could be accumulated from the sample were only sufficient for identification purposes. The extracted organic compounds were found to be remarkably similar to humic acid extracted from leonardite that occurs in North Dakota (8). These humic acid extracts contain long-chain carboxylic acids as well as sulfur and nitrogen groups. Cyanidation of oxidized ore in the presence of humic acids showed that $Au(CN)_2^-$ was adsorbed or associated with the humus compounds and that gold recovery was essentially nil.

It was concluded that the low extraction of gold from the carbonaceous materials could not be attributed wholly to physical adsorption of the $Au(CN)_2^-$ complex on carbon, but that in certain of these materials, a substantial amount of the gold was locked in in the form of a chelate containing CO-N-S ligands.

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CHEMICAL OXIDATION OF CARBONACEOUS ORES

LABORATORY EXPERIMENTS

The data indicated that destruction or complete pacification of detrimental carbon components is a requisite for effectively extracting gold from the various carbonaceous materials. It was determined that a mild chemical oxidation of the carbonaceous ores followed by cyanidation yielded high gold extraction. Various oxidation systems were investigated, including ozone, chlorine, NaOCl, calcium hypochlorite [$Ca(OCl)_2$], permanganates, perchlorates, chlorates, and oxygen. Gold extraction, obtained by cyanidation after oxidation, increased significantly in nearly every case over that obtained without pretreatment (6-7).

The use of ozone as an oxidant was further investigated (9). It was determined that 95 pct Au extraction could be obtained from several different carbonaceous ores by slurrying the ore with brine solution, lowering the pH to 1 with H_2SO_4 or HNO_3, and bubbling ozone through the slurry. After the ozone treatment was completed, the gold was extracted by cyanidation. However, owing to the acid-consuming calcareous nature of the ore, the ozone system, in which an acid medium was used, was ruled out as an impractical solution to the carbonaceous problem.

Introduction of chlorine gas into an ore slurry, followed by filtering and subsequent cyanidation of the filter cake, resulted in 95 pct Au extraction from several carbonaceous ores (7). Rapid addition of the chlorine gas (as represented below) caused the pH of the ore pulp to drop to the range of pH 1 to 2.

$$Cl_2 + H_2O \rightarrow HCl + HOCl. \quad (A)$$

However, the pH remained neutral with slow addition of chlorine gas because the HCl formed reacted slowly with the calcareous gangue material to give $CaCl_2$:

$$2HCl + CaCO_3 \rightarrow CaCl_2 + H_2CO_3. \quad (B)$$

The active oxidizing species obtained from rapid addition of chlorine gas is principally HCl. Slow addition of chlorine gas results in production of $Ca(OCl)_2$ as the principal oxidizing species:

$$2HOCl + CaCO_3 \rightarrow Ca(OCl)_2 + H_2CO_3. \quad (C)$$

The amount of chlorine gas that escapes from the pulp can be excessive. To overcome this problem, NaOH or lime was added to the slurry before the addition of chlorine gas. The chlorine gas reacts with the base to form $Ca(OCl)_2$ or NaOCl:

$$Cl_2 + 2NaOH \rightarrow NaOCl + NaCl + H_2O, \quad (D)$$

$$2Cl_2 + 2Ca(OH)_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O. \quad (E)$$

The hypochlorite or oxidizing species then reacts with carbonaceous material in the ore, passivating activated-type carbon and breaking hydrocarbon chains and humic acid-type components.

Since the NaOCl (household bleach) proved to be an effective oxidizing agent, the parameters affecting gold extraction were investigated. It was determined that 90 pct Au extraction could be obtained at 50° C in 4 h using 16 to 20 lb NaOCl per short ton of ore along with 20 lb/st of lime (7).

Instead of adding NaOCl or chlorine to the ore pulp, the oxidizing condition could be produced by slurrying the ore in brine and electrolyzing to produce NaOCl in situ. A literature survey indicated that the technology for the electrolysis of NaCl in ore slurries was essentially nonexistent. Preliminary experiments indicated that oxidizing conditions could be generated and controlled under a variety of conditions by this electrooxidation concept (10-11). Parameters deemed to be important to the development of the technique included salt concentration, electrolysis time at constant amperage per short ton of ore, temperature, current density, type of electrodes, electrode spacing, and particle size of ore (7).

During the course of the investigation it was determined that a variety of electrode materials and configurations could

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be used. The only difficulty encountered was a buildup of a deposit on the cathode with time. This difficulty was overcome by using graphite electrodes and reversing the current periodically to remove the deposits. One type of cell used, a plate-type laboratory-scale electrooxidation cell, is shown in figure 2.

The effect of salt concentration (NaCl) on gold extraction from carbonaceous ore was investigated. It was determined that an 8- to 10-pct-salt concentration was adequate for obtaining sufficient oxidation to result in efficient gold extraction by cyanidation.

The effect of temperature on gold extraction was determined through tests at 30°, 40°, and 50° C. Maximum gold extraction was obtained at 40° C. Heat input to an electrooxidation system and the resulting temperature are functions of the conductivity of the electrolyte and the power required to accomplish the oxidation; therefore, parameters such as electrode spacing, salt concentration, and pulp density are all critical in maintaining the desired temperature. Generally speaking, electrode spacing should be as close as is consistent with good pulp flow between electrodes. The effect of increasing electrode spacing was investigated. Spacings of 3/8, 5/8, and 1-1/8 in were used, with pulp density at 40 pct and a salt concentration of 10 pct. As was expected, the resistance between the electrodes increased with increased electrode spacing. The effect of pulp density on conductance was also studied (fig. 3). As was expected, the conductance decreased rapidly as pulp density increased.

Current density is another factor that affects the voltage-amperage relationship, which in turn affects the temperature. The effect of current density on the voltage required to maintain constant amperage during electrolysis is shown in figure 4. The voltage increased linearly with current density over the range measured. The data indicated that the current density should be as low as possible to keep power consumption at a minimum. However, the current density dictates the number of electrodes required, and the tonnage of the mill and the size of the agitators employed are important factors that must also be considered in projecting the number of electrodes that can be practically utilized.

Grinding is an important part of any hydrometallurgical process; it releases

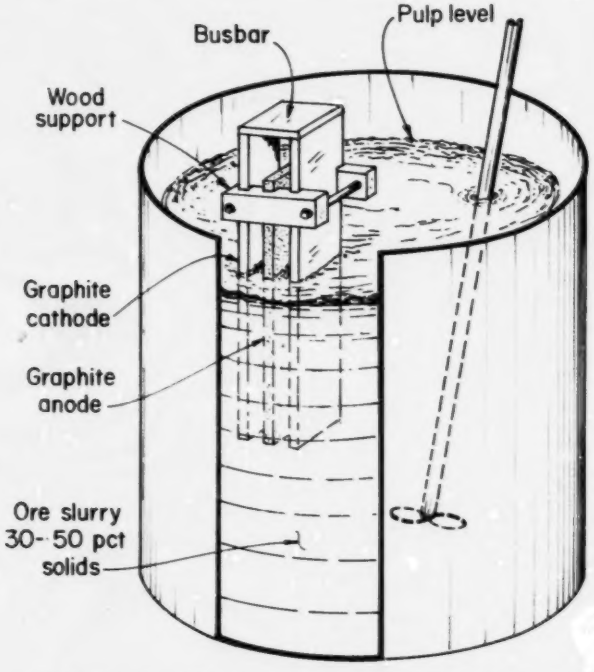

FIGURE 2. - Plate-type laboratory-scale electrooxidation cell and agitation vessel.

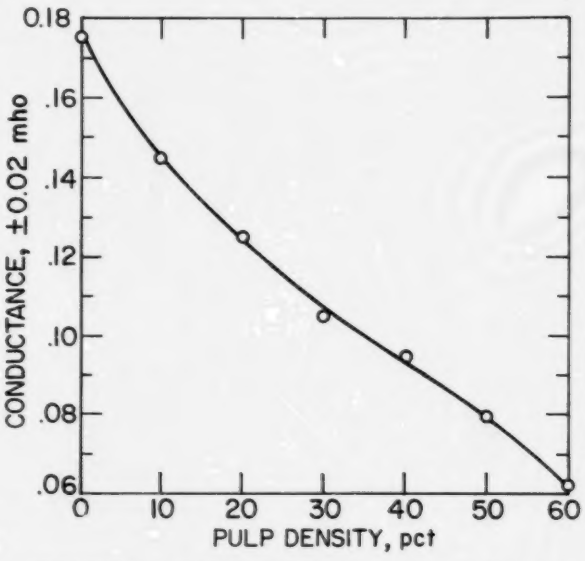

FIGURE 3. - Effect of pulp density on conductance in ore-brine pulp (using 9.77-pct-salt solution).

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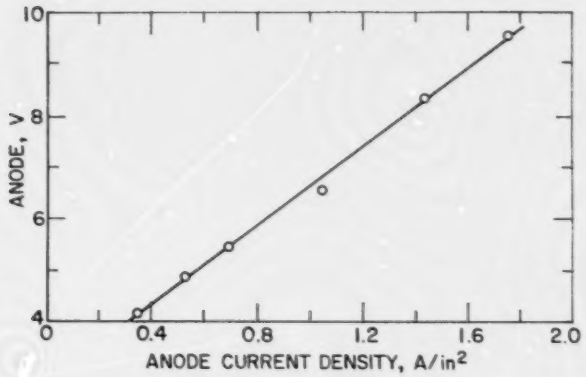

FIGURE 4. - Effect of anode current density on voltage at constant amperage.

the mineral from the host rock so the mineral can come in contact with the reactants. The effect of particle size on gold extraction was investigated using several different grinds based on the percentage of minus 200-mesh material. Data for one ore indicated that gold extraction increases as the particle size becomes smaller and that a grind of 70 pct minus 200 mesh was satisfactory; however, each ore must be evaluated on an individual basis as to optimum particle size for reaction.

PILOT PLANT STUDIES

Based on the results obtained in laboratory studies, the use of NaOCl and chlorine and the in situ generation of NaOCl (electrooxidation) were investigated on a pilot plant scale (12-13). The ores used in these studies were obtained from the Carlin Gold Mine. The flow sequence and pilot plant operation generally followed conventional countercurrent-decantation slime-circuit operating practice. Ore material was ground to 60 pct minus 200 mesh at 50 pct solids in the rod mill and pulped into the oxidation tanks, each of which held 275 lb of dry ore (550 lb of pulp). After treatment in the oxidation tank at the desired temperature, the pulp was passed through the digestion-surge tank, where 1 lb of cyanide per short ton of ore was added, along with sufficient lime to maintain a cyanidation pH of 11. Approximately 5 lb of lime per short ton of ore was usually required to maintain the desired pH value. The pulp was then pumped through three cyanidation tanks, for a cyanidation time of 9 h. From the cyanidation tanks the pulp passed through four thickeners at 20 pct solids, flowing countercurrent to the barren solution recycled from the gold-precipitation sequence. Pregnant solution was passed from the first thickener to the gold-precipitation system.

Initial pilot plant experiments were conducted on nonrefractory oxide gold ore to determine the best operating conditions for the grinding circuit and pulp handling, optimum flow rates, etc. Mill tails from the oxide ore contained 0.008 tr oz/st Au, which corresponds to a gold extraction of 96 pct.

Carbonaceous gold ore was processed in the pilot mill, using conventional cyanidation, without oxidation pretreatment, as a baseline experiment to determine the effect of carbonaceous material. Gold extraction obtained in these experiments ranged from 29 to 33 pct (0.26 to 0.28 tr oz Au per short ton of tails).

Oxidation by NaOCl Addition

The pilot plant operations generally followed the operating conditions established in the laboratory experiments for obtaining favorable gold extraction values. The oxidation section of the plant was operated on a semicontinuous basis with ground ore being treated on a batch basis in successive oxidation tanks. The ore then could be discharged into the surge tank in such a manner that a reserve of treated pulp was available for continuous operation of the cyanidation and liquid-solids separation sections of the mill. The oxidation section of the mill processed 80 lb of dry ore per hour, thus providing a retention time of 9 h in the cyanidation tanks.

Figure 5 shows the oxidation results--the gold extractions obtained at different levels of NaOCl addition to the pulp containing carbonaceous ore. As shown in figure 5, the reaction time, temperature, and lime addition were kept constant. The pulp pH values were in the 11 to 11.5 range. Extraction increased markedly

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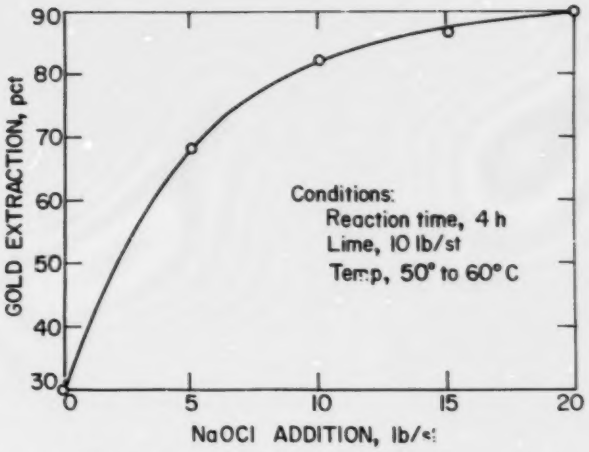

FIGURE 5. - Effect of NaOCl addition on gold extraction.

with addition of 5 to 10 lb/st NaOCl and then increased gradually with larger NaOCl additions. Gold extraction by subsequent cyanidation reached 90 pct with a 20-lb/st-NaOCl addition. The results closely paralleled similar laboratory experiments conducted on a different sample of carbonaceous gold ore.

In other experiments, a reaction time of 3 h (instead of 4 h) was shown to be sufficient when 20 lb of lime per short ton was used. It was also determined that the optimum temperature for oxidation with NaOCl lies between 50° and 60° C.

Oxidation by Chlorine Addition

Addition of chlorine to a pulp of finely ground carbonaceous ore and water was investigated as a means of producing hypochlorite oxidant in situ on an economical and easily controlled basis. As chlorine is bubbled into the pulp, it reacts with water to form HOCl and HCl. These products are buffered by the calcareous gangue in the ore to form $Ca(OCl)_2$ and $CaCl_2$. Oxidation of the carbonaceous matter is thought to be accomplished by the hypochlorite ion.

It had been shown in the laboratory experiments that addition of chlorine gas at moderate rates to the agitated pulp through a sintered-disk sparger resulted in favorable oxidation without excessive loss of chlorine gas. The chlorine reacted rapidly, and gold extraction from the oxidized pulp by subsequent cyanidation was shown to be largely independent of the rate of chlorine addition. The factor limiting the rate of chlorine addition appeared to be the amount of hypochlorite remaining after oxidation. The hypochlorite product reacted with the carbonaceous matter as chlorine was added during the initial stages of the oxidation, and no hypochlorite could be detected in the solution. The amount of hypochlorite in solution increased with time until the oxidation was completed. It was determined that the oxidation can be completed in as little as 4 h; however, at this relatively rapid rate of chlorination, the $Ca(OCl)_2$ in solution can increase to 1 pct or more in the later stages of oxidation. If hypochlorite is allowed to rise to a level that cannot be consumed by the ore, it will consume cyanide in the cyanide circuit. Therefore, it is desirable to limit the $Ca(OCl)_2$ in solution to less than 0.2 pct during chlorination. This resulted in a chlorination time of up to 15 h at 24° to 30° C for some of the more refractory samples, with an additional 5 h for the ore to consume the residual hypochlorite. The final concentration of $Ca(OCl)_2$ going to cyanidation was less than 0.02 pct.

Pilot plant tests were run with three 55-gal drums connected in series, each containing 275 lb of solids at 40 pct solids. Chlorine was fed to each drum through a 1/2-in-diam pipe extending to the bottom of the drum. Oxidation was conducted on a batch basis with the pulp overflow from the third tank being continuously recirculated through the system to give the desired chlorination time. The near-optimum temperature of 24° to 30° C was maintained by heating the pulp. The pH of the system remained at 6.6 during chlorination without adjustment. Figure 6 shows that gold extraction increased rapidly with increasing chlorine addition. The optimum extraction 92 pct, was obtained using 40 lb/st chlorine.

Scale-up experiments were conducted in a 6- by 7-ft tank containing 7.5 st of pulp at 40 pct solids. Chlorine gas was bubbled in through four pipes submerged

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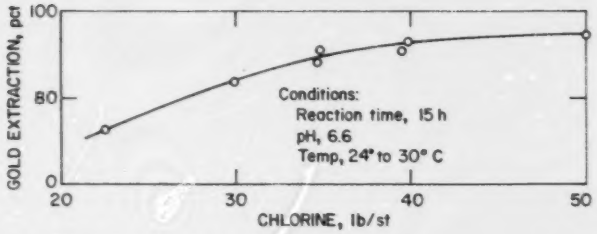

FIGURE 6. - Effect of chlorine addition on gold extraction.

5 ft into the tank. Chlorine was added over an 8-h period at the rate of 3.5 lb/(st·h) initially, then decreased to 1.5 lb/(st·h) over the last 2.5 h. Gold extractions of 89 pct (0.035 oz Au per short ton of tails) were obtained using 38 lb/st chlorine. These results paralleled those obtained in the pilot-plant-scale experiments.

Electrooxidation of Carbonaceous Ores

In additional pilot plant studies, electrolysis used on ore pulp prepared from finely ground carbonaceous ore and salt brine was investigated as a means of generating oxidizing conditions in situ. The cell used was a simple plate-type arrangement consisting of graphite electrodes 2-1/2 in wide, 3/4 in thick, and 30 in long (fig. 7). Identical graphite cathodes and anodes were placed alternately in a nonconductive holder with 1/2-in spacing, which allowed favorable pulp flow through the system.

The pilot plant investigations determined the effect of temperature on gold extractions, the effect of salt concentration on gold extractions and power requirements, and the effect of electrode spacing at various salt concentrations on power requirements. The data obtained were similar to the data obtained in previous laboratory tests. Gold extractions of 90 pct were obtained using 10-pct-salt concentrations at 40° C, a current density of 0.67 A/in^2, and an electrode spacing of 1/2 in.

Scale-up experiments were conducted on a batch basis using a 6- by 7-ft agitator tank capable of holding 7.5 st of pulp at 40 pct solids. Electrooxidation was accomplished with two banks of graphite

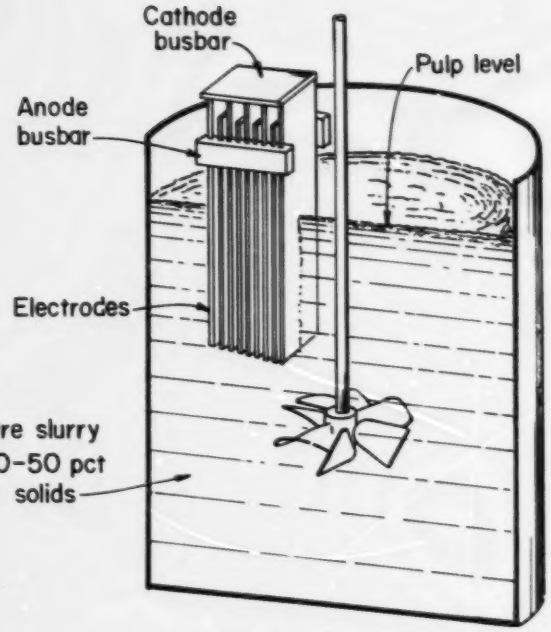

FIGURE 7. - Plate-type electrode assembly for direct electrolytic production of NaOCl in ore slurry.

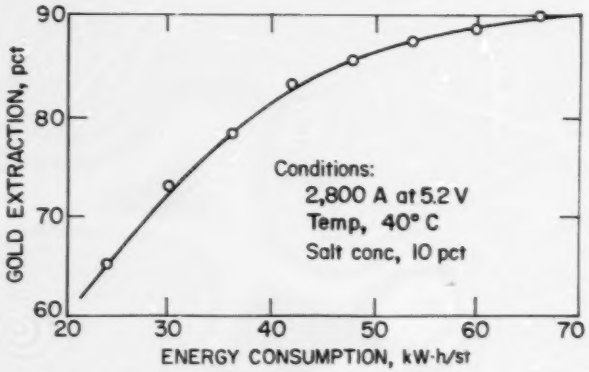

FIGURE 8. - Gold extraction and energy consumption for large-scale experiments.

electrodes used in parallel, each containing 12 anodes and 11 cathodes. Tests were conducted at 40° C, with a 2,800-A current and a 10-pct-salt concentration in the pulp solution. Oxidized pulps were not cyanided in the pilot plant, but samples were taken at 1-h intervals and cyanided on a bench scale. Figure 8 shows that gold extraction increased with electrolysis time, reaching a maximum extraction of 89.4 pct, which corresponded to 22 h of electrolysis. Data obtained

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from the larger experiments indicated that scale-up to commercial plants should not present any serious problems.

The pilot plant studies were a cooperative effort of the Newmont Mining Corp.'s Carlin Gold Mine and the Bureau of Mines. Experiments were conducted at the Carlin Gold Mine and at the Bureau's Reno (NV) Research Center. Based on the results of the testing program, the Carlin Mine installed a full-scale facility using chlorine to treat carbonaceous ores prior to cyanidation.

CONCLUSIONS

Treatment of carbonaceous gold ores from north-central Nevada with NaOCl or chlorine, or by electrolytic oxidation resulted in favorable gold recovery by subsequent cyanidation. The gold that is complexed by humic acid-type compounds was liberated, and the adsorptive properties of the ore were passivated by the oxidation treatment. Gold extractions in the 90-pct range were obtained on several tonnage ore samples from the Carlin Gold Mine. Equivalent metallurgical performance, compatible with present plant practice, was obtained with NaOCl, chlorination, and electrooxidation. The choice of one of these methods is therefore dictated by economic conditions such as the cost and availability of electric power, NaOCl, and chlorine.

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CARBON ADSORPTION-DESORPTION

By J. A. Eisele[1]

ABSTRACT

The Bureau of Mines has developed three methods for stripping gold and silver from activated carbon that enable the carbon to be reused many times. These three desorption techniques are to strip the precious metals with either (1) boiling NaOH-NaCN solution at atmospheric pressure; (2) NaOH-NaCN solution at temperatures above boling, in pressure vessels; or (3) an NaOH-NaCN solution containing ethyl alcohol at temperatures below boiling. All three methods are widely applied in industry. This paper describes the three methods and their development.

INTRODUCTION

The introduction of cyanide leaching in the 1890's revolutionized the processing of gold and silver ores. Since that time, the standard hydrometallurgical process to recover gold and silver from disseminated ores has become cyanide leaching in a countercurrent decantation (CCD) plant (1).[2] The operation of a conventional CCD plant (fig. 1) consists of the following steps:

1. The ore is crushed and ground.
2. During grinding, the ore is slurried with dilute basic cyanide solution typically containing 0.1 pct NaCN and enough CaO to maintain a pH range of 10 to 11.
3. The slurry is agitated in a series of leaching tanks to give a total leaching time of 12 to 48 h, depending on the characteristics of the ore.
4. The slurry is thickened and washed countercurrently in a series of thickeners.
5. The pregnant solution from the first thickener is clarified by filtration and deaerated by vacuum.
6. Zinc powder is added to precipitate the gold and/or silver.
7. The gold-silver-zinc sponge is filtered and refined to bullion.
8. The barren cyanide solution is returned to the washing-leaching circuit, and makeup cyanide and base are added.

Gold and silver recovery from pregnant solutions by zinc precipitation can present problems. Ideally, the pregnant solution should be clear before precipitation, and it must be deaerated. This can be difficult to achieve with slimy ores. Also, precipitation is an inefficient method for recovering gold from dilute solutions. Different forms of carbon, especially activated carbon, have long been known to be good adsorbers of gold and silver cyanides from solution. However, since the only known means to recover the gold and silver from the carbon was to burn it, carbon was not used extensively. In a few cases, where slimy ores were being treated, gold adsorption on carbon was the preferred method for

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[2]Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

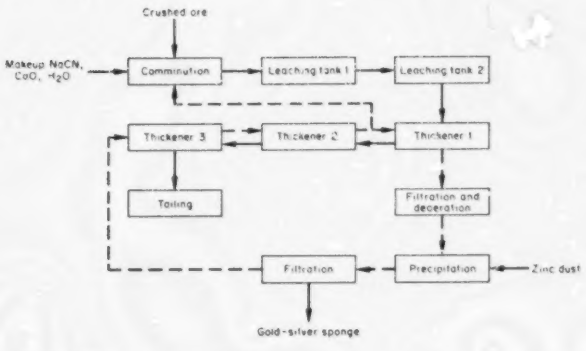

FIGURE 1. - Flow diagram of countercurrent decantation cyanide leaching plant.

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recovering the precious metal values because the clarification step was eliminated. The precious-metal-loaded carbon was recovered from the slurry by screening or flotation.

USE OF BOILING NaOH-NaCN SOLUTION

In the late 1940's, Bureau of Mines researchers were looking for ways to strip the precious metals from loaded carbon to enable the carbon to be reused a number of times. A World War II surplus of activated carbon manufactured from fruit pits was available at prices that made using carbon cheaper than using zinc. A means for desorbing and recycling the carbon would make carbon adsorption a very economical process for the recovery of gold. In 1950, an alkaline Na_2S stripping method was described that eluted the gold, but not the silver, from carbon (2). As most ores contain some silver, and silver in some ores is the primary value, the sulfide stripping method was not satisfactory because the carbon would eventually be loaded with unstrippable silver. In 1952, Bureau researchers reported a method for desorbing gold and silver from loaded carbon (3). Precious metals were stripped by contacting the carbon with a boiling NaOH-NaCN solution. With each pass of the solution through the carbon bed, some of the gold and silver was removed. After being passed through the carbon bed, the solution entered an electrolysis cell, where the remaining gold and silver were deposited on the cathode. The barren solution was then reheated and recycled through the carbon. A 1 pct NaOH-0.1 pct NaCN solution at its boiling point desorbed more than 90 pct of the gold and silver in 4 to 6 h. The carbon could be reused up to 10 times without losing significant activity.

Carbon adsorption-desorption-electrowinning permitted gold and silver recovery from slimy ores or the slimy portion of ores by eliminating the requirement of a clarified solution. This became the foundation for two important developments in gold and silver ore processing: carbon-in-pulp (CIP) cyanidation and heap leaching. The cylindrical electrolytic cell originally described (2) is still used for electrowinning and is commonly referred to as a "Zadra" cell, even though many units in commercial use have been modified. Rectangular electrowinning cells are also used, to make better use of floor space than cylindrical cells. The NaOH-NaCN electrolyte and steel wool cathode remain common to all gold-silver electrowinning cells. The Bureau's desorption-electrowinning process, known as the Zadra process, has been utilized in cyanide milling for more than 30 yr.

Although gold and silver were eluted from the fruit pit carbon in 4 to 6 h in pilot-scale tests, this was not the general case. Commercial practice, which had adopted harder carbons made from coconut shells, showed that 24 to 48 h was required to desorb more than 90 pct of the precious metals using alkaline cyanide solution heated to boiling. Although this was better than not being able to strip the carbon, the long stripping time was undesirable. Bureau research was directed toward ways to decrease the stripping time. Two methods, pressure stripping and alkaline-alcohol stripping, were developed; both greatly decreased the desorption time.

PRESSURE STRIPPING AND ALKALINE-ALCOHOL STRIPPING

In 1973, Bureau researchers showed that by using a pressure vessel and increasing the temperature of the stripping solution, gold could be stripped from carbon in 2 to 6 h (4). The loaded carbon was conditioned with caustic-cyanide solution at 90° C and eluted with water at 150° C. One advantage was that consumption of cyanide and caustic was less with heated pressure stripping than it was using prolonged ambient pressure stripping. The stripping solution was cooled to 90° C and the gold recovered by electrowinning.

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In the alkaline-alcohol stripping method, developed by Bureau researchers in 1976, ambient pressure was used, but the modified stripping solution contained 20 pct ethanol in addition to the alkaline cyanide (5). At 80° C, gold and silver were desorbed in 6 h. A concurrent development was the separation of gold from silver by precipitating silver as a sulfide (6). The separation of silver as a sulfide takes place after desorption from the carbon and results in a purer gold bullion. For pregnant solutions containing considerable amounts of silver, the preferable sequence is to precipitate the silver before loading the carbon (7). A large carbon inventory is avoided by maintaining capacity for only gold adsorption. The Ag_2S precipitate can be smelted to a silver bullion. The gold in the filtrate from silver precipitation is adsorbed, desorbed, and electrowon.

SUMMARY

Pressure stripping, alkaline-alcohol stripping, and ambient pressure stripping are all used by industry to strip gold and silver from activated carbon. Using any of these three methods, the carbon can be reused many times. The preference of the mill operator is the determining factor in choosing the stripping system.

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HEAP LEACHING

By J. A. Eisele[1]

ABSTRACT

The Bureau of Mines began investigating heap leaching in 1969 in an effort to provide a low-cost means for recovering precious metals from ores that were too low in grade to be economically processed by conventional cyanide technology. By 1979, the Bureau had developed an agglomeration pretreatment method that permitted heap leaching to be applied to clayey and finely divided materials. Today, heap leaching is widely used by the mining industry. This paper briefly describes and discusses heap leaching and agglomeration pretreatment.

INTRODUCTION

Heap leaching was first used on oxide copper ores and uranium ores (1).[2] It had the advantages of very low capital cost, low operating costs, and operational flexibility. Bureau researchers proposed heap leaching in 1969 as a low-cost means for recovering gold values from disseminated gold ores with porous gangue, mine stripping waste, and submarginal ores (2-4). Heap leaching has since become an important factor in precious metals recovery because it permits utilization of lean ores and wastes that cannot be economically processed by conventional agitation cyanidation. Fifteen years after the method's introduction, there are between 50 and 100 commercial gold and silver heap leaching operations, ranging in size from 10 st/wk to 10,000 st/d.

LEACHING

In heap leaching, the crushed ore material is piled in heaps on impervious pads. A dilute alkaline-cyanide solution is distributed on top of the heap by a sprinkling system. The solution percolates through the heap and drains from the impervious pad. The pregnant gold solution from the heap typically contains from 1 to 3 ppm Au.

For many operations, precipitation of the metal values with zinc is not the most efficient recovery method. Another method, carbon adsorption, is very efficient for recovering of metals from dilute solutions. The pregnant solution is passed through a series of columns containing activated carbon, and the gold is adsorbed. The resulting barren solution is fortified with reagents and recycled to the heap. Leaching continues until the gold extraction is completed. The gold-loaded carbon is stripped by carbon adsorption or zinc precipitation. Some pregnant solutions from silver heap leaching contain enough silver, typically 10 to 20 ppm Ag, that zinc precipitation can be used to recover the silver.

For heap leaching to be feasible, the ore must be porous and permeable to the leaching solution. Since the ore is not finely ground, the cyanide ions must diffuse through the host rock to dissolve a gold particle. The dissolved gold must diffuse outward. This requires leaching cycles weeks or months long, and may result in dissolved gold cyanide complexes that are not completely washed from the heap. Runoff from abandoned heaps is not discharged to surface or groundwater sources until the effluent from the spent heap is free of cyanide. A flow diagram of a typical heap leaching operation is shown in figure 1.

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[2]Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

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PRETREATMENT

Although application of the heap leaching technique to gold and silver ores permitted development of many low-grade and/or small properties that otherwise would not have been exploitable, some ores were untreatable by heap leaching. This was due to two conditions: (1) The ore contained clay, which swelled on contact with the leaching solution, blocked the voids in the heap, and thereby prevented solution flow; and (2) the ore, after crushing to the liberation size for gold-silver extraction, generated an unusually large amount of fines (minus 200 mesh) that were washed into the voids by the percolating leaching solution, causing channeling and incomplete leaching of the gold and silver from the heap material.

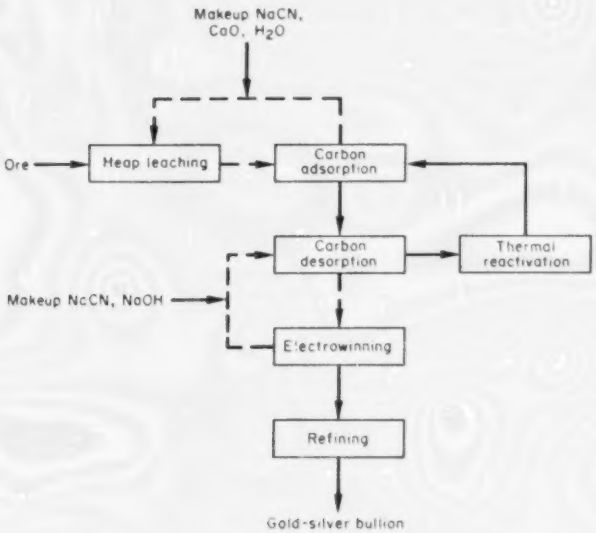

FIGURE 1. - Flow diagram of heap leaching.

In 1979, Bureau researchers published a report describing an agglomeration method that was successful in overcoming these problems (5-6). Agglomeration as a pretreatment for heap leaching consists of (1) mixing the crushed ore with portland cement, which acts as a binding agent, and lime to provide alkalinity; (2) wetting the mixture evenly with solution, which may contain cyanide to start leaching before the heap is built; and (3) mechanical tumbling of the mixture so the fine particles adhere to the larger particles. Several hours of aging are needed for the cement to bond the particles. When stable bonds are formed, the agglomerates are very durable and resistant to degradation. This simple pretreatment has increased the flow of some ores through the columns as much as 6,000-fold and, in actual heaps, has decreased the leaching cycle to days instead of weeks. It is estimated that half of the heap leaching operations use some type of agglomeration pretreatment (7). Agglomeration pretreatment can also be applied to finely divided material such as tailings or finely ground ore (8). The conditions required to form good agglomerates are more rigorous, but when the criteria are met, it is possible to process finely divided low-grade and/or small resources.

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THE CARBON-IN-PULP PROCESS

By Stephen D. Hill[1]

ABSTRACT

This paper briefly reviews the development of the carbon-in-pulp (CIP) process for recovering gold and silver from cyanide leach solutions. A brief history and a description of the various steps in the process are presented. Reference is made to published research findings, from both the Bureau of Mines and other sources, that contributed significantly to commercial development and utilization of the process.

INTRODUCTION

The application of activated carbon to recover gold and silver from cyanide leach solutions was patented as early as 1894 (1).[2] T. G. Chapman, of the University of Arizona, is credited with the original development of CIP processing in the late 1930's. In Chapman's system, the dissolved gold was adsorbed by finely ground activated charcoal. Subsequently, the charcoal was separated from the pulp by flotation, and gold was recovered from the charcoal by burning or smelting (2).

In an alternative system, Chapman used larger particles of activated carbon, particles that were much coarser than the ground ore, as the gold adsorbent. The carbon, enclosed in a cylindrical screen basket, was circulated and rotated within the leach pulp. A concentrated gold solution was obtained by stripping the gold-loaded carbon with hot cyanide solution (3). Bureau of Mines researchers further modified the Chapman system in the early 1950's by adding an electrolytic cell for continuous removal of gold from the hot strip liquor (4).

A small commercial CIP plant was operated from 1954 to 1960 at the Golden Cycle Corp.'s Carlton Mill in Cripple Creek, CO. In that operation, coarse carbon in screen baskets was loaded with gold to about 40 tr oz/st Au, then stripped and recycled by the Zadra method (5).

In 1970, the Homestake Mining Co. discontinued mercury amalgamation in its milling plant in Lead, SD, because of downstream pollution. Since the ore had a high slime content, Homestake's difficulties provided an opportunity for the Bureau to test its own concepts for improved gold extraction, loading, and carbon handling in a modified cyanide CIP system. Research in these areas was performed under a cooperative agreement between the Bureau and Homestake. At the time, conventional plants used a costly system for processing low-grade, lode gold ores that contained finely disseminated gold. Considerable capital investment was required for fine grinding, agitation leaching in cyanide solution, countercurrent decantation in thickeners for solid-liquid separation, residue washing, clarification of pregnant solution by filtering, vacuum deaeration, and precipitation of the gold by reacting the solution with zinc powder.

The alternative system, proposed by the Bureau, optimized the following operations: pulp leaching, CIP loading, carbon separation, stripping, electrowinning, and carbon regeneration. The innovative system was perfected and demonstrated at Homestake in a miniplant that handled 2 st/d of slime pulp. By extrapolation of the design from the miniplant, Homestake was able to start its

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[2]Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

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commercial CIP plant, treating 2,000 st/d slime, in 1973 (6). Bureau metallurgists reported on the Homestake project and the new CIP process at the American Mining Congress Mining Convention in Denver, CO, the same year (7).

The Bureau subsequently developed the carbon pressure stripping process, and refinements were made in a new design for the electrowinning cell. Cost data presented in 1974 clearly showed that the CIP system was superior to the conventional countercurrent decantation system (8). The MINTEK organization in Johannesburg, Republic of South Africa, began work on CIP in 1976, and many significant developments have resulted from its intensive efforts (9).

Other CIP plants patterned after the Bureau process include Duval Corp.'s Battle Mountain, NV, operation in 1978 (10); Pinson Mining Co.'s Winnemucca, NV, plant in 1980 (11); and Freeport Gold Co.'s operation near Elko, NV, in 1981, the largest plant of its kind in the United States (12). Getty Mining Co., Mercur, UT, started a carbon-in-leach (CIL) plant, an offshoot from the CIP process, in 1983 (13). Today, the CIP process is the standard of the gold industry throughout the world, with 30 plants in North America, 10 plants in Australia, and approximately 20 plants in the Republic of South Africa using the process (14-16).

LEACHING

The CIP process, shown in figure 1, includes cyanide agitation leaching, countercurrent carbon-pulp contact, and carbon-pulp separation. The leaching step of the process, usually accomplished in a multistage system, comprises several tanks; four to six stages are typical. The ore, normally ground to minus 100 mesh or finer, is leached in a thick slurry of about 45 to 50 pct solids. Lime or caustic is added to maintain protective alkalinity. To speed up gold dissolution, the pulp is vigorously aerated and agitated during leaching. The retention time necessary for complete

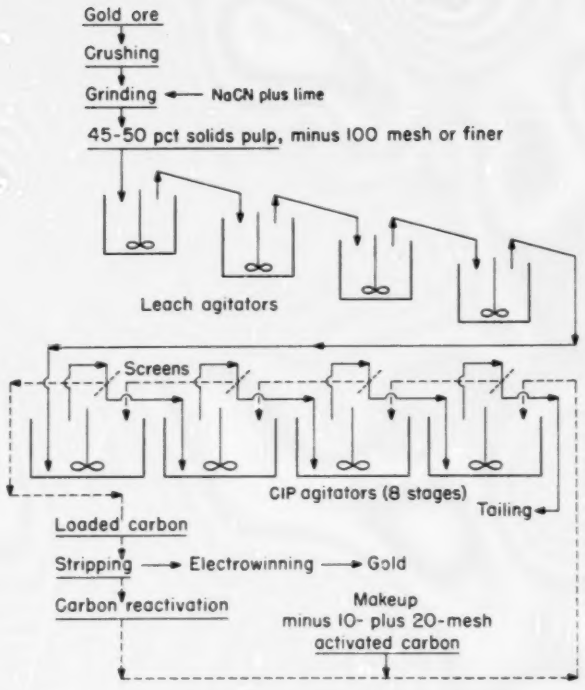

FIGURE 1. - CIP process.

dissolution of the gold depends greatly on the particle size of the gold, but 2 to 24 h is typical. Other factors that influence the rate of dissolution include particle size of the ore, clay content, pulp density, pH, cyanide strength, temperature, and slurry viscosity.

The Dorr agitator, with a slow-speed center sweep and either peripheral or center-column airlifts, has worked well on finely ground ores. Pachuca tanks also have been successful; they may be capable of handling a coarser feed than the traditional Dorr tanks. A draft tube-type agitation tank has also been used successfully. The type of vessel most suitable for CIP processing depends on the type of ore being treated and the prevailing operating conditions. In most cases, a deep tank with turbine-type mechanical agitators and low tip speeds is preferred (17). Dissolution of gold and silver is essentially completed before the leached pulp moves to the CIP adsorption circuit.

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ADSORPTION

The CIP adsorption circuit is a cascade of agitated vessels through which the pulp flows by gravity. In each vessel, the pulp is contacted with carbon granules that preferentially adsorb gold and silver from the solution as the pulp overflows from one vessel into the next. Periodically, a portion of the carbon inventory is transferred up the cascade to the next vessel by airlifting a quantity of carbon-bearing pulp. The transfer system is abrasive; therefore, coconut shell activated carbon is generally used because it is resistant to abrasion. There is some variation in the size of carbon particle used. The only strict criterion for carbon size is that particles be large enough to allow easy separation from the pulp; a minus 6- plus 16-mesh carbon size is quite common.

The optimum loading of gold and silver on the carbon is generally a matter of economics and is very dependent on metal prices. Consideration must be given to the ore grade, solution value, gold inventory, and security. Frequent stripping and handling can result in lower loading, so most large operations usually load the carbon to 200 to 400 tr oz/st Au before the carbon is removed from the first tank in the cascade.

Several factors influence the adsorption capacity of gold onto activated carbon from cyanide solutions. Some of the more important are the ionic strength and pH value of the solution, temperature, the presence of competing metal ions and poisons, and the nature of the carbon. In addition, a number of factors influence the extraction rate of gold cyanide from activated carbon in the stirred tanks, the most important of which are the mixing efficiency in the tanks, pulp viscosity, and carbon granule sizes (18).

The Bureau of Mines recommends that adsorption efficiencies be determined by conducting laboratory CIP batch tests to obtain adsorption rate data and establish equilibrium isotherms (19-20). These adsorption rates and equilibrium curves can then be used to design the optimum adsorption system.

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CARBON SEPARATION

Methods of separating the loaded carbon particles from the gold-depleted pulp are numerous and widely varied. In early CIP circuits, screen baskets or external vibrating screens were used extensively. A vibrating screen with a minus 20- plus 24-mesh stainless steel square mesh deck has proven to be reliable. Such screens have worked well at a number of plants without malfunctioning.

A problem of carbon fines being generated caused operators to look for improved methods that would save power, reduce fine carbon generation, and reduce capital costs. The new concepts that resulted include either a peripheral screen or a submerged launder-type screen that fits across the top of the CIP tank. Typically there are two or three such launders on each tank. Each launder has two or three removable screens set in the side panels, which may be vibrated for carbon transfer, if necessary.

CARBON-IN-LEACH

Leaching generally requires a much longer pulp residence time than adsorption. Consequently, it is possible to reduce the equipment requirement in the CIP circuit by using the leach vessels for both cyanidation and adsorption simultaneously, thus eliminating the need for a separate adsorption cascade. Such a system is called a carbon-in-leach (CIL) circuit (21). Because the activated carbon adsorbs gold and silver from solution, not from the ore, there are advantages in partially preleaching the ore before adsorption starts. Leaching can go on in the presence of carbon that is moving countercurrent to the flow of pulp, similar to the operation of a standard CIP circuit.

RECOVERY OF GOLD AND SILVER

The activated carbon, loaded with gold and/or silver, may be shipped to a smelter to recover the precious metal values. Such a procedure is sometimes used, particularly for small mines whose

capital is limited and reserves are small. However, for better economy in larger operations, the carbon is preferably stripped, reactivated, and reused in the process. Details of carbon stripping, regeneration, and recovery of precious metals by electrowinning from strip solution are discussed in other papers in this Information Circular.

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PRECIOUS METALS RECOVERY FROM ELECTRONIC SCRAP AND SOLDER USED IN ELECTRONICS MANUFACTURE

By B. W. Dunning, Jr.[1]

ABSTRACT

Electronic scrap from obsolete and/or damaged avionics or from manufacturing sources poses a problem for the owner or generator of the scrap in terms of its fair value. The complexity of this material, as well as the low concentration of precious metals (generally less than 1 pct), makes it difficult to obtain a representative sample for assay. The owner or generator is therefore dependent on the reliability and competence of a toll refiner to obtain a fair value. The Bureau of Mines has investigated various procedures for either concentrating precious metals from electronic scrap into an easily assayable form or for recovering fairly pure gold, silver, or platinum-group metals (PGM). Procedures the Bureau has studied are described and discussed in this paper, including hand dismantling, mechanical processing, pyrometallurgy, hydrometallurgy, and electrometallurgy.

INTRODUCTION

Gold, silver, and PGM are widely used in electronic and electrical components to provide long-term reliability. Fabrication of equipment used by the military consumes the largest portion of precious metals used in the electronics and electrical industry. The disposal of obsolete and/or damaged military electronics (reportedly totaling more than 10,000 st/yr) at a fair value is a pressing problem for the Department of Defense (DOD). This is partly due to the highly variable and complex nature of military electronic scrap, which makes it difficult to obtain a homogeneous sample for precious metals analysis. Private industry has the same problems, but faces fewer constraints in dealing with them.

The Bureau of Mines, in cooperation with DOD, the National Association of Recycling Industries (NARI), and others, has developed many procedures for determining precious metals content in scrap. However, some of these procedures are not economical except under special circumstances. Initial research to determine precious metals content in electronic scrap relied on hand dismantling and object recognition. Subsequent studies investigated mechanical processing as a method for obtaining metal concentrates containing the major portion of the precious metals. In later studies, these precious metal concentrates were treated using various procedures, including pyrometallurgy, hydrometallurgy, and electrometallurgy, to further concentrate or recover the precious metals. These procedures are discussed in the following sections, and data concerning the effectiveness of each procedure are presented.

HAND CHARACTERIZATION OF SELECTED AVIONIC MODULES (1-2)[2]

In 1977, the Defense Property Disposal Service (of the DOD) initiated a test recovery program that included having the Bureau of Mines hand-process a controlled sample lot containing a variety of "black boxes" (surplus electronic units so

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[2]Underlined numbers in parentheses refer to items in the list of references at the end of this paper.

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designated because of their black outer cases). The program was to include determination of base and precious metals content, removal of salable modules, and a monetary evaluation of each box. Several identical lots were prepared with components intact to assure a basis for direct comparison. The Bureau received one lot of boxes for hand dismantling to determine the potential yield of base and precious metals from each unit. An identical lot of boxes was placed on display at the Defense Construction Supply Center, Columbus, OH, for private industry to bid on determination of the following:

1. Relative cost-effectiveness of and estimated cost per item for currently practicable methods for precious metals segregation, identification, and recovery and for serviceability testing of usable modules from individual boxes.

2. Reutilization and sales potential of usable modules and components, with sales potential supported by quotations from prospective purchasers.

All interested industry groups indicated that the sample lot was too low in value to warrant bidding and too old for reutilization of usable modules. More than half of the sample consisted of radio receivers, transmitters, tuners, and power supplies; the remainder consisted of miscellaneous navigational and communication equipment. All units appeared to have been produced prior to 1957 and did not contain any printed circuits. The weights for individual units in the sample lot ranged from 2-1/2 to 58 lb. The total weight of the sample lot was 726 lb. The avionic units came from the military aircraft storage located in the Arizona desert near Tucson. A summary of the materials composition of the 36 hand-dismantled avionic units is listed in table 1.

MECHANICAL PROCESSING OF ELECTRONIC SCRAP AND GOLD AND SILVER DISTRIBUTION IN THE VARIOUS FRACTIONS (3-5)

Approximately 5 st of general avionic scrap "black boxes" was mechanically processed through a series of unit operations. These unit operations included a hammer mill, air classifier-baghouse, magnetic separator-trommel, vibrating screen, rolls crusher, wire separator screen, magnetic precleaner, eddy-current separator, and high-tension separator. The various materials recovered from these unit operations and their distribution are listed in table 2, along with the assay and the amount of gold and silver in each material fraction. Three material fractions, the lights, wire bundles, and the metallics from high-tension separation, contained most of the gold and silver. It was determined that these materials, representing 34 pct of the original 5 st, could be economically processed by a toll refiner to obtain credit for the precious metals.

Hand-segregated printed cards and electrical plugs and connectors were also processed through a modified series of mechanical unit operations. Rolls crushing and magnetic precleaning were not deemed necessary for processing these items. The amount and distribution of materials recovered from circuit cards using the various unit operations are shown in table 3, along with the assay and the amount of gold and silver in each material fraction; the results shown are from processing approximately 920 lb of printed-circuit cards.

The amount and distribution of materials recovered from mechanically processing some 600 lb of electrical plugs and connectors are listed in table 4, along with the assay and the amount of gold and silver in these components. Most of the gold and silver was found in the high-tension metal and baghouse lights.

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TABLE 1. - Summary of materials composition of hand-dismantled avionics units, weight percent

Unit[1]	Aluminum base	Copper base	Magnetic metals	Stainless steel	Nonmetals	Fraction containing precious metals[2]
Receiver-transmitter	20.4	35.8	19.1	4.3	20.3	14.5
Tuner, radio.....	57.3	20.8	9.5	4.4	7.9	13.5
Tuner, radio.....	56.8	20.1	9.1	5.3	8.6	13.4
Tuner, radio.....	54.9	17.6	10.5	7.5	9.5	11.6
Radio receiver.....	25.1	28.3	29.0	2.3	15.3	11.1
Converter.....	47.4	23.5	11.0	3.2	14.8	8.2
Keyer.....	28.5	23.6	21.0	5.7	21.2	5.2
Amplifier.....	32.9	22.2	23.8	2.3	18.7	5.2
Video amplifier.....	29.4	23.5	19.3	8.9	18.9	4.7
Video decoder.....	51.6	13.3	11.5	8.5	15.1	3.6
Radio receiver.....	28.6	25.9	23.5	1.5	20.4	3.5
Receiver-transmitter	56.6	17.0	13.5	1.3	11.5	2.8
Control transmitter.	32.1	22.4	12.9	13.7	18.9	2.8
Video coder.....	54.3	16.0	9.0	3.4	17.3	2.8
Indicator.....	39.5	12.8	12.9	3.9	30.9	2.6
Tuner, radio.....	59.6	16.5	8.3	5.5	10.1	2.5
Tuner, radio.....	62.1	12.4	8.3	8.5	8.8	2.3
Tuner, radio.....	61.8	14.7	9.3	5.9	8.3	2.3
Tuner, radio.....	51.2	17.7	14.1	7.9	9.1	2.2
Receiver.....	34.5	17.4	26.7	1.7	19.6	2.2
Coder transmitter set.....	45.3	15.3	22.5	1.4	15.5	2.2
Receiver-transmitter	36.4	18.8	23.1	3.3	18.3	1.9
Azimuth indicator...	36.2	19.8	21.1	4.4	18.5	1.8
Receiver.....	25.9	21.7	30.1	3.4	18.9	1.8
Receiver-transmitter	32.0	17.7	21.2	3.4	25.7	1.5
Indicator.....	43.9	17.0	19.6	3.0	16.5	1.4
Azimuth indicator...	40.2	17.5	20.8	4.3	17.1	1.3
Power supply.....	27.9	19.0	31.1	2.3	19.7	1.3
Receiver-transmitter	28.8	18.1	28.6	4.0	20.5	1.2
Power supply.....	6.3	24.4	47.6	2.5	19.2	1.1
Power supply.....	28.6	16.8	34.5	.6	19.4	1.0
Power supply.....	25.1	15.9	33.3	3.7	21.9	.8
Storage unit.....	58.4	14.1	15.7	.5	11.3	.3
N[1] compass.....	16.1	5.1	43.8	33.3	1.7	.2
Inverter.....	32.6	19.4	41.4	.8	5.8	.2
Electron tube.....	14.3	8.4	69.4	5.5	2.3	0

[1]Where units of the same kind are listed more than once, each listing represents an individual unit.

[2]Percentage of the total black box weight that contained precious metals, based on hand segregation of silver- and gold-coated components through visual examination.

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TABLE 2. - Material distribution, concentration, and weight of contained precious metals from fractions of mechanically beneficiated general avionic scrap

Fraction	Weight, lb	Distribution, wt pct	Concentration, wt pct		Contained precious metals, tr oz	
			Au	Ag	Au	Ag
Baghouse lights.....	930	8.9	0.021	0.33	2.8	44.7
Wire bundles.....	860	8.2	.021	.77	2.6	96.6
Magnetics:						
Minus 1/2 in.....	1,204	11.5	.015	.07	2.6	12.3
Minus 1 plus 1/2 in....	1,825	17.4	([1])	([1])	([1])	([1])
Eddy-current:[2]						
Precleaner magnetics...	425	4.0	.064	.41	4.0	25.4
Aluminum.....	1,161	11.1	ND	.017	ND	2.9
Middles.....	965	9.2	.003	.64	.42	90.1
High-tension metal:[3]						
Minus 1/4 in.....	552	5.3	.099	2.01	8.0	161.7
Minus 1/2 plus 1/4 in..	444	4.2	.074	1.96	4.8	127.0
Minus 1 plus 1/2 in....	773	7.4	.031	1.09	3.5	122.9
High-tension rejects (minus 1 in)[3].....	1,318	12.6	.017	.30	3.3	57.7
Hammer-mill knockout box contents.....	23	.2	([4])	([4])	([4])	([4])
Composite, total or average.....	10,480	100.0	.021	.48	32.02	741.3

ND Not detected.

[1]Visual observation of this fraction showed no evidence of precious metals except for a few large power transistors.

[2]Fractions obtained using ramp-type eddy-current separator.

[3]Fractions obtained using high-tension separator.

[4]Not determined.

TABLE 3. - Material distribution, concentration and weight of contained precious metals in fractions of mechanically beneficiated printed-circuit cards

Fraction	Weight, lb	Distribution, wt pct	Concentration, wt pct		Contained precious metals, tr oz	
			Au	Ag	Au	Ag
Baghouse lights.....	214.6	23.2	0.075	0.61	2.35	19.1
Wire bundles.....	11.2	1.2	.068	.97	.11	1.6
Magnetics (minus 1/2 in).	283.6	30.7	.030	.05	1.24	2.1
Eddy-current aluminum (minus 1/2 in).....	16.6	1.8	ND	.01	ND	.02
High-tension metal (minus 1/2 in).....	324.9	35.2	.150	1.55	7.11	73.4
High-tension rejects (minus 1/2 in).....	72.0	7.8	.023	.37	.24	3.9
Composite, total or average.....	922.9	99.9	.082	.74	11.05	100.1

ND Not detected.

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TABLE 4. - Material distribution, concentration, and weight of contained precious metals in fractions of mechanically beneficiated electrical plugs and connectors

Fraction	Weight, lb	Distribution, wt pct	Concentration, wt pct		Contained precious metals, tr oz	
			Au	Ag	Au	Ag
Baghouse lights.....	81.6	13.6	0.081	0.88	0.96	10.5
Wire bundles.....	6.6	1.1	.043	1.34	.04	1.3
Magnetics (minus 1/2 in).	53.2	8.9	.020	.10	.16	.78
Eddy-current aluminum (minus 1/2 in).....	66.6	[illegible]	ND	.015	ND	.15
High-tension metal (minus 1/2 in).....	199.8	33.3	.137	1.12	3.99	32.6
High-tension rejects (minus 1/2 in)[1].....	191.8	32.0	ND	ND	ND	ND
Composite.....	599.6	100.0	.059	.52	5.15	45.3

ND Not detected.

[1]Visual observation of the high-tension rejects (minus 1/2 in) indicated that the shattered pieces of plastic, ceramic, hard rubber, and other types of insulator material contained no precious-metals-bearing contact pins after shredding.

In processing either whole avionic units or hand-segregated circuit cards, electrical plugs, and connectors, the greatest amount of gold and silver is always concentrated in the high-tension metal product. Most of the remaining gold and silver concentrates in the wire and baghouse lights. These fractions are best handled by a toll refiner. A toll refiner will first incinerate these fractions separately to remove the organics. After incineration, the high-tension metal product and wire are dissolved in a molten heel of copper. The melt is then thoroughly mixed and cast into ingots for assay of the precious metals. The baghouse lights are also incinerated, then ball or rod milled; the resulting powder is then blended, coned, quartered, and assayed.

HYDROMETALLURGICAL RECOVERY FROM ELECTRONIC SCRAP

GOLD AND SILVER FROM HIGH-TENSION METALLIC FRACTION (6-7)

The high-tension metallics from mechanically processed avionic units, representing about 17 pct of the units' total weight, contained slightly more than 50 pct of the total gold and silver. The high-tension fraction, with its high surface-area-to-weight ratio, is ideal for upgrading by leaching. The elemental composition of this fraction is listed in table 5. The major base metals in the high-tension fraction were copper, aluminum, and iron, in that order. Aluminum is removed by leaching with 20-wt-pct NaOH. After washing, the residue is countercurrently pressure leached in three stages with 20-vol-pct H_2SO_4 to remove the copper.

TABLE 5. - Elemental composition of high-tension metallic fraction from avionic scrap

	Conc, wt pct		Conc, wt pct
Ag.....	1.37	Fe.....	9.4
Al.....	27.2	Ni.....	3.2
Au.....	.12	Pb.....	.2
Cr.....	.1	Sn.....	2.1
Cu.....	38.4		

NOTE.--Remainder was mostly Si as SiO_2 (fiberglass and plastic filler).

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The distribution of metal values in the leach solutions and in the residues is listed in table 6. Copper is recovered from the pregnant leach liquor by cementation with transformer steel from the coarse magnetic fraction of mechanically processed avionics. The cement copper is a good grade and assays better than 90 pct.

TABLE 6. - Concentration and distribution of metal values in leach solutions and residues

Elements	Leach solutions		Residues	
	Conc, g/L	Distribution, pct	Conc, wt pct	Distribution, pct
Ag.....	<0.001	<0.004	8.13	99.1
Au.....	ND	ND	.74	>99.9
Cr.....	.0004	6.2	.42	94.0
Cu.....	36.3	89.3	24.4	10.9
Fe.....	2.9	29.0	39.6	71.0
Ni.....	1.02	38.8	9.0	61.1
Pb.....	.003	1.4	1.1	98.6
Pd.....	ND	ND	.21	99.9
Sn.....	.14	7.9	9.5	91.1

ND Not detected.

Silver is recovered from the pressure-leached residue by dissolution in 50-vol-pct HNO_3 and subsequent precipitation with NaCl as AgCl. This AgCl is reduced to silver metal by mixing with Na_2CO_3 and heating to 600° C. Copper not extracted during H_2SO_4 leaching is recovered from the silver-free HNO_3 leach solution by cementation with steel scrap. Gold is extracted from the HNO_3 leaching residue with aqua regia and precipitated with $NaHSO_3$. Analyses of the gold and silver products and the final residue is listed in table 7. The final residue consisted mostly of acid-insoluble noncombustibles (mostly silica), stainless steel, and tin.

PLATINUM-GROUP METALS (8)

Hydrometallurgical techniques have also been investigated as a means for recovering platinum-group metals from electronic scrap.

Telephone Relay Scrap

NARI estimates that about 1,000 st/yr of telephone relay scrap is available for processing. Palladium, gold, and platinum are found in the contact points, which are brazed to cupronickel wires. These contact points represent approximately 0.06 pct of the modular weight. Mechanical processing, including shredding, air classification, magnetic separation, screening, and high-tension separation (HTS), produced an HTS metallic fraction containing most of the relay contact points. A portion of this HTS concentrate representing 8.7 pct of the original scrap was pressure leached in stainless steel autoclaves in a two-stage countercurrent arrangement with solid-liquid separation between each stage. The purpose of the first-stage leach was to react fresh HTS concentrate with the second-stage liquor to produce a pregnant liquor with a low concentration of H_2SO_4 (less than 10 g/L). Partially leached solids from the first-stage leach were fed to the second stage, where they were leached with a fresh H_2SO_4-HNO_3 solution. Measured quantities of HTS-PGM concentrate (usually 120 g), 1 L of H_2SO_4 solution (20 vol pct), and HNO_3 (20 mL to 120 g concentrate) were charged to the autoclave and heated to 90° C with a 100-lbf/in^2 air overpressure. Air was sparged through the autoclave (about 10 bubbles per second) during all leaches. After leaching, the slurry was removed from the autoclave and filtered, and the products were analyzed. Increasing the reaction time from 1 to 4 h increased base metal extraction from 96 to 99 pct. Quantitative analyses of the residue and filtrate are listed in table 8. The residue, representing 0.2 pct of the HTS-PGM concentrate, was suitable for shipping to a toll refiner for recovery of silver, gold, and PGM.

Reed Switches

NARI sources estimate that approximately 10 st of reed switches, a valuable scrap material, is available for processing annually. Reed switches consist of

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TABLE 7. - Semiquantitative spectrochemical analyses of products from pressure-leached residue, weight percent

Element	Product		Final residue
	Gold	Cement silver[1]	
Ag	0.03 - 0.3	>10	0.0003- 0.003
Al	.003- .03	0.03 - .3	.3 - 3
Au	>10	.0003- .003	ND
Cr	.003- .03	ND	.3 - 3
Cu	.003- .03	.03 - .3	.1 - 1
Fe	.03 - .3	.03 - .3	.3 - 3
Ni	.003- .03	.003 - .3	.01 - .1
Pb	.01 - .1	.3 - 3	.1 - 1
Pd	1 - 10	ND	ND
Si	.1 - 1	.1 - 1	>10
Sn	.03 - .3	.3 - 3	1 - 10

ND Not detected.

[1]Quantitative analysis of remaining cement silver after semiquantitative spectrochemical analysis, in weight percent: 97.5 Ag, 0.028 Al, 0.53 Cu, 0.12 Pb, and 1.82 Sn.

TABLE 8. - Quantitative analyses of residue and filtrate from leaching telephone relays

Element	Concentration	
	Residue, wt pct	Filtrate, g/L
Ag	1.3	0.001
Au	14.8	.0004
Cu	1.3	67.9
Cr	<.003	.0003
Mn	ND	.03
Ni	.09	14.4
Pd	77.7	.0007
Pt	.29	.009

ND Not detected.

two magnetizable reeds with their extremities fused in a glass envelope. The inner ends of the reeds are plated with gold and then rhodium. A simple rolls crushing step followed by magnetic separation of the reeds from the glass powder was the only preprocessing necessary to prepare the reed switches for hydrometallurgical treatment. Assay of the reed switches showed them to be, in weight percent, 49 Co, 48 Fe, 2 V, 0.5 Au, and 0.4 Rh.

The approach to recovering gold and rhodium from this scrap was to dissolve the cobalt-iron substrate in either HCl (1:1) or HNO_3 (1:2) using ultrasonic agitation. Dissolution of the base-metal substrate was relatively fast except for the working face of the reed plated with gold and rhodium. Complete removal of base metals required 12 h of continuous leaching. The insoluble residue was a fine gold-rhodium sand assaying approximately 50 pct Au and 50 pct Rh. A spectrochemical analysis of the gold-rhodium sand is listed in table 9. Gold was readily removed from the Rh with aqua regia, leaving a pure 99.8-pct-Rh sand. Recovery of the gold was accomplished by precipitating with $NaHSO_3$; however, other methods of recovering the gold are available. The byproduct metals cobalt and vanadium can be recovered from the iron-cobalt-vanadium solution using existing technology.

TABLE 9. - Semiquantitative spectrochemical analysis of gold-rhodium sand from reed switches

Element	Conc, wt pct	Element	Conc, wt pct
Ag	0.003- 0.03	Mn	0.001- 0.01
Al	.003- .03	Pb	.003- .03
Au	>10	Rh	>10
Co	.03 - .3	Si	.01 - .1
Fe	.01 - .1	Sn	.03 - .3
Mg	.001- .01		

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COPPER CEMENTATION WITH SELECTED MATERIALS FROM AVIONIC SCRAP (9)

A process using either brittle aluminum base or magnetic metallics from electronic scrap as a copper precipitant in acidulated $CuSO_4$ solution was developed to separate and then upgrade a high-grade cement copper containing all or most of the precious metals. Aluminum-bearing obsolete avionic assemblies and plugs and connectors removed from electronic scrap were incinerated and then melted and cast to form brittle ingots. An assay of these incinerated and melted items is listed in table 10. The brittle ingots were broken up and rolls-crushed to minus 35 mesh. Copper cementation took place when this material was agitated in the acidulated $CuSO_4$ solution in a countercurrent system. The precipitate contained better than 90 pct Cu and all of the associated precious metals. The cement copper thus obtained can be beneficiated by fire refining to produce high-grade anode material for subsequent electrorefining to cathode copper. An anode mud is produced from which the precious metals can be recovered using standard procedures.

TABLE 10. - Analyses of ingots produced by incineration and melting of military electronic scrap

	Plugs and connectors	Avionic assemblies
Analysis, tr oz/st:		
Ag	196.8	157.0
Au	87.43	0.16
Concentration, wt pct:		
Al	48.5	38.4
Cu	37.2	24.0
Fe	3.4	26.3
Mn	0.13	(1)
Ni	0.84	(1)
Zn	3.2	0.23
Insol	5.1	4.7

[1]Not determined.

The magnetic fraction of shredded electronic scrap, which is mostly thin silicon steel laminae from transformers, is an excellent copper cementation agent when it is agitated in an acidulated $CuSO_4$ solution. It also contains nickel-alloy transistor caps that contain some gold and silver. A representative sample of the magnetic fraction from shredded electronic scrap was melted, cast, and sampled for assay. An assay of this material is listed in table 11.

TABLE 11. - Analysis of a representative sample of shredded magnetic scrap

	Value
Analysis, tr oz/st:	
Ag	7.2
Au	5.96
Concentration, wt pct:	
Cr	0.7
Cu	0.7
Fe	75.8
Ni	11.5
Insol	4.4

Copper cementation was most efficient when shredded magnetic scrap was used in a tumbler-type system, since a vigorous scrubbing action was needed to maintain the precipitation reaction. An analysis of the combined precipitate showed it to contain, in weight percent, 89 Cu, 1.1 Fe, 0.32 Pb, 0.36 Sn, 1.5 insolubles, and in ounces per short ton, 4.0 Au and 11.5 Ag.

The total precipitate was melted in an induction furnace without flux. An anode, representing 90 pct of the charge weight, was obtained from the melt; the balance, containing most of the impurities, remained as a sinter. The anode was placed in a polypropylene sock and electrorefined in a solution containing 150 g/L H_2SO_4 and 40 g/L Cu at a current density of 12 A/ft^2. Previous electrorefining tests using these conditions produced a dense, smooth cathode deposit. Assays of the various products are listed in table 12. The anode mud can be further refined using standard procedures for gold and silver recovery.

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TABLE 12. - Analyses of electrorefining products

	Anode	Cathode[1]	Anode mud
Analysis, tr oz/st:			
Ag.....	12.1	ND	1,140
Au.....	4.3	ND	412
Analysis, pct:			
Cu.....	99.4	99.9	57.0
Fe.....	0.13	ND	ND
Pb.....	0.104	ND	0.7
Sn.....	0.047	ND	0.316
Insol.....	0.05	ND	NS

ND Not determined.

[1]A spectrographic analysis of the cathode copper showed the following impurities (estimated): 0.001 wt pct Mg and 0.01 wt pct Ca.

TABLE 13. - Analyses of products obtained from melting and electrolytically solubilizing unreacted magnetic scrap residue

	Residue[1]	Anode mud	Solution, g/L
Analysis, tr oz/st:			
Ag.....	35	239	NA
Au.....	12	129	NA
Analysis, wt pct:			
Co.....	0.7	NA	1.9
Cr.....	0.5	NA	0.9
Cu.....	11.0	55.0	0.05
Fe.....	40.0	17.0	50
Ni.....	46.4	18.0	61
Insol.....	Na	8.0	NA

NA Not analyzed.

[1]Cleaned, unreacted scrap residue.

The cleaned, unreacted residue from the copper cementation with shredded magnetic scrap (amounting to 11.0 pct of the original charge) was melted in an induction furnace and cast into an anode. An assay of the metal is listed in table 13.

The anode was suspended in a electrolytic cell fitted with a graphite cathode and partially solubilized in an electrolyte containing 150 g/L H_2SO_4. The metals in solution (table 13) could be treated by presently used technology to recover the nickel, cobalt, and chromium. The anode mud (table 13) can be treated using standard procedures for the recovery of the precious metals.

SWEATING AVIONIC SCRAP TO PRODUCE ALUMINUM BULLION FOR FUSED SALT ELECTROLYSIS (10)

The Bureau developed and tested two molten-salt electrorefining procedures for processing aluminum ingots sweated from avionic scrap in order to recover a high-quality aluminum and concentrate the gold and silver in the aluminum-depleted anodes. An analysis of one of the ingots is listed in table 14.

One system used a three-layer cell. The three molten layers were separated because of differences in the densities of the molten anode material, the molten salt electrolyte, and the molten refined aluminum. At the operating temperature range of 750° to 850° C, the approximate density was 3.3 g/cm^3 for the molten electronic scrap, 2.7 g/cm^3 for the molten electrolyte, and 2.3 g/cm^3 for the molten refined aluminum. The electrolyte contained, in weight percent, 60 $BaCl_2$, 17 NaF, and 23 AlF_3. The recovered aluminum had a purity of 99.8 pct. The composition of the anode residue from the three-layer cell (representing 33 pct of the electronic scrap ingot) is listed in table 15. The anode residue can be readily refined to copper bullion suitable for further treatment by aqueous acid electrolysis to separate precious metals and copper.

TABLE 14. - Composition of electronic scrap ingot

	Value
Analysis, tr oz/st:	
Ag.....	119
Au.....	12
Concentration, wt pct:	
Al.....	69.69
Cu.....	19.98
Fe.....	0.50
Mg.....	0.13
Mn.....	0.20
Ni.....	0.22
Pb.....	1.07
Si.....	2.57
Sn.....	1.19
Zn.....	4.02

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TABLE 15. - Composition of total anode residue, three-layer cell

	Value
Analysis, tr oz/st:	
Ag	378
Au	37
Concentration, wt pct:	
Al	6.93
Cu	61.61
Fe	2.03
Mg	0.007
Mn	0.32
Ni	0.61
Pb	1.88
Si	6.48
Sn	6.75
Zn	10.16

A second system used a compartmented cell that provided separate compartments for the anode and cathode metals instead of the density separation used in the three-layer cell. The cell was operated in the range of 750° to 800° C. The electrolyte consisted of an equimolar mixture of NaCl and KCl, with enough $AlCl_3$ to provide a 1- to 2-wt-pct Al concentration in the electrolyte. The recovered aluminum had a purity of 99.6 pct. The composition of the anode residue from the compartmental cell (representing 32 pct of the electronic scrap ingot) is listed in table 16. This anode residue can also be refined to copper bullion suitable for electrorefining. The two fused-salt electrorefining processes are technically feasible; however, economic evaluations have not been made.

TABLE 16. - Composition of total anode residue, compartmental cell

	Value
Analysis, tr oz/st:	
Ag	365
Au	35
Concentration, wt pct:	
Al	12.2
Cu	60.9
Fe	1.66
Mg	<0.01
Mn	0.45
Ni	0.68
Pb	3.27
Si	8.04
Sn	3.64
Zn	7.77

INCINERATION, CAUSTIC LEACHING, SMELTING, AND ELECTROREFINING OF AVIONIC SCRAP (11)

From a metallurgical standpoint, avionic scrap is a complex mixture of various metals, mostly copper, aluminum, and iron, attached to, covered with, or mixed with diverse types of plastics and ceramics. Precious metals occur as platings of various thicknesses, in relay contact points, on switch contacts and wires, and in solders.

The plastics and organics can be eliminated prior to smelting by incineration at 400° to 500° C in a gas-fired furnace. The furnace must be equipped with an afterburner and a scrubber in order to meet antipollution regulations. Iron alloys are removed with a drum magnet. The aluminum content, generally about 35 to 40 pct in avionics, may be removed by caustic leaching with regeneration of the caustic. Leaching is not necessary unless there is a ready market for the Al_2O_3. Smelting of the incinerated scrap, with or without the aluminum removed, is done to produce a homogeneous assayable product that can be sold to a custom smelter. An ingot produced from electronic scrap, without the aluminum removed, assayed 30 wt pct Cu, 18 wt pct Fe, and 32 wt pct Al, and 120 tr oz/st Ag and 1 tr oz/st Au. Smelting another batch of electronic scrap low in aluminum produced an ingot that assayed 85 wt pct Cu, 4 wt pct Fe, and 0.2 wt pct Al, and 333 tr oz/st Ag and 26 tr oz/st Au. These two assays illustrate the heterogeneity of electronic scrap composition. The remelted ingots, with or without the aluminum removed, can be further refined by slag additions and blowing air through the melt. The resulting copper bullion is refined electrolytically, and the anode slimes, which are rich in precious metals, are sent to a toll refiner for final processing.

Economic evaluation of the various procedures for processing avionic scrap

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indicates that incineration followed by smelting to form an assayable ingot and selling this product to a custom electrorefiner is the most cost-effective procedure.

TREATMENT OF SPENT TIN-LEAD SOLDER FROM MANUFACTURE OF ELECTRONIC PRINTED CIRCUIT CARDS TO RECOVER GOLD (12-13)

Estimates indicate that 2,000 st of spent solder containing about 120,000 tr oz Au is generated annually (12). One method for recycling the tin-led solder and recovering the gold is fused-salt electrolysis (12). Electrorefining of the spent solder is carried out at 450° to 500° C with a molten KCl-$SnCl_2$-$PbCl_2$ electrolyte. The spent solder is charged to the anode container. Both anode and cathode electrodes are tungsten. Electrolyte composition is, in weight percent, 14 KCl, 28 $SnCl_2$, and 58 $PbCl_2$. The electrolyte melting point is 390° C. Refined tin-lead solder is recovered at the cathode. In tests, gold at the anode increased from about 60 to 2,200 tr oz/ st. The impure gold bullion collected at the anode is treated by conventional fire refining to recover relatively pure gold.

A second method for recycling spent tin-lead solder is by drossing with aluminum or zinc (13). The electronic solders used in studying this method were nominal 60-40 tin-lead solders that had become so contaminated during wave soldering of printed circuit boards that they would no longer form acceptable bonds. The analyses of two contaminated solders used in the drossing study are listed in table 17.

TABLE 17. - Analyses of some as-received scrap electronic solders, parts per million

Element	Lot 1	Lot 2
Ag.....	110	179
Al.....	<25	<25
Au.....	1,785	2,361
Bi.....	<200	<20
Cu.....	1,900	1,350
Fe.....	(1)	244
Ni.....	(1)	68
Sb.....	1,250	1,250
Si.....	200	<30
Zn.....	19	19

[1]Not determined.

Recovery of gold from electronic solders by phase separation requires a density difference between the solder and the drossing agent. Scrap electronic solders have specific gravities ranging from 8.45 to 8.85 g/cm^3, while the specific gravities of aluminum and zinc are 2.70 and 7.14 g/cm^3, respectively.

Samples of scrap solder were melted in open clay and clay-graphite crucibles in a conventional pot furnace. Bath temperatures were held at 550° C for aluminum-treated solders and at 350° C for zinc-treated solders. Agitation of the bath during cooling helped phase separation. When the bath temperature reached 200° to 250° C, the dross was removed from the solder by filtering.

In addition to gold, the aluminum also removes significant amounts of antimony, copper, iron, and nickel from the solder, but is not effective for silver removal. Zinc is as effective as aluminum for removing gold from solder and also removes silver, copper, iron, and nickel, but not antimony. The use of zinc, however, imposes distinct disadvantages. Compared with aluminum, approximately eight times as much zinc, on a molar basis, is needed to completely remove gold from the solder. Zinc dross does not become as viscous as aluminum dross as the bath temperature is lowered, thus complicating phase separation. In addition, solder dissolved larger quantities of zinc than aluminum, making it more difficult to repurify the solder to an acceptable electronic grade. Therefore, in general, aluminum drossing is preferred over zinc drossing except for solders containing substantial quantities of silver.

Dross recovered by filtration contains essentially all of the gold originally present in the solder and typically represents about 10 pct of the weight of the solder. This dross can be further processed to concentrate the gold, since about 85 pct of the dross is entrained solder.

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Heating the dross in the range of 800° to 1,000° C will oxidize aluminum and aluminum-gold compounds together with some of the lead and tin. Most of the metallic solder entrained in the dross, amounting to 15 to 40 wt pct of the dross, remains in the metallic state and is separated from the oxidized material by grinding and screening. The metallic portion remains on a 200-mesh screen, whereas the oxidized material passes through. The entrapped solder recovered from the dross has approximately the same concentration of gold as the original scrap solder and is recycled when a fresh batch is treated.

The gold in the oxide phase is in the free metallic state and can be reclaimed by aqua regia digestion or by a combined cyanidation-amalgamation procedure. If aqua regia digestion is chosen, the base metal oxides should first be treated to remove them so they do not report to the aqua regia with the gold. This is best accomplished by leaching the oxides successively with a 50-pct NaOH solution and concentrated HCl. The NaOH solution removes most of the Al_2O_3, while HCl dissolves the remaining soluble impurities. After filtering and washing, the solutions are discarded. The remaining solids are treated in two steps with aqua regia, then filtered and washed. Approximately 98 pct of the gold dissolves in the aqua regia. Gold can be recovered from the aqua regia solution by conventional cementation procedures. In cemented form, the gold can be easily processed by a gold smelter for final purification.

The second technique utilizes combined cyanidation-amalgamation. Neither cyanidation nor amalgamation alone is effective because of the variation in the size distribution of the gold particles. The larger particles are removed by amalgamation, while the smaller particles are dissolved by the cyanide solution. In order to use the combined cyanidation-amalgamation procedure, the oxides must first be treated with 5N HNO_3. This treatment is necessary to remove a tarnished surface film from the gold that hinders reaction of the gold with the cyanide solution or with mercury. HNO_3 also dissolves unoxidized solder and some base metal oxides. Combined cyanidation-amalgamation is generally preferred over aqua regia digestion because of the highly corrosive nature of aqua regia, which complicates the selection of construction materials.

CONCLUSIONS

Efforts to recover precious metals from electronic and electrical scrap will benefit from initial hand segregation of the scrap material, in nearly every case, even if the segregation is only minimal. Base metals recovered will usually pay for the segregation step. Mechanical processing of electronic and electrical scrap by companies specializing in this operations is available on a toll basis. The material fractions obtained from mechanical processing are homogeneous enough for assaying. Assays enable the generator or owner to determine whether the scrap has enough value to at least pay for shipping and toll refining charges. The Bureau's studies in electronic and electrical scrap recovery have shown that mechanical processing to obtain homogeneous materials for assaying is beneficial and economical, and a study conducted by private industry has borne out this conclusion. However, further processing to recover precious metals is best handled by toll refiners.

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